ELSEVIER

Catalysis Today 62 (2000) 241–247

CATALYSIS TODAY

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Structure/function relationships for basic zeolite catalysts containing occluded alkali species

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Abstract

The basicity and reactivity of alkali-modified zeolites were investigated in order to elucidate the role of occluded species on catalytic activity. To synthesize intrazeolite oxide or metal species, cesium acetate or cesium azide was impregnated into the pores of zeolites and decomposed in situ. To characterize the basicity of the samples, we used adsorption of iodine and carbon dioxide. The blue shift in the UV–visible spectrum of adsorbed iodine was found to increase with increasing electropositivity of the exchangeable cation, indicating greater donor strength of the zeolite framework. Cesium-exchanged zeolite X was an active catalyst for the reaction of ethylene oxide and carbon dioxide to form ethylene carbonate. For a series of faujasite-type zeolites with different loadings of occluded cesium oxide, the CO_2 uptake increased linearly with the amount of occluded Cs. The catalytic activities of the CsO_x/CsX samples for the isomerization of 1-butene and dehydrogenation of 2-propanol increased linearly with the amount of excess cesium, consistent with results from the adsorption of CO_2. A majority of the base sites on these materials exhibited a heat of CO_2 adsorption around 85 kJ mol^{-1}, which is much lower than the 270 kJ mol^{-1} seen on bulk cesium oxide. After thermal pretreatment, Na(azide) and Cs(azide) modified X zeolites catalyzed the side-chain alkylation of toluene with ethylene and the side-chain alkenylation of *o*-xylene with butadiene, whereas occluded cesium oxide was inactive in the reactions. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Zeolite; Cesium; 1-Butene; 2-Propanol

1. Introduction

Relatively little is known about the active sites for solid bases, despite their potential as environmentally benign, industrial catalysts. Solid bases are now recognized as effective catalysts for a range of organic transformations such as double-bond isomerization of olefins, side-chain alkylation of aromatics, dehydrogenation of alcohols and Knoevenagel condensation of aldehydes [1–5].

Alkali metals and metal oxides are among the strongest bases. Both rubidium and cesium oxide have been reported to be "superbases", possessing a Hammett basicity function exceeding +26 [6]. These materials have a very low surface area that limits their ability to be effective catalysts. Therefore, it is believed that supporting these metals and oxides on high surface area carriers like zeolites would give materials exhibiting strong basicity.

Ion-exchanged zeolites have been used to catalyze many reactions known to occur over a base site, like toluene alkylation with methanol. Occlusion of alkali metal oxide clusters in zeolite cages via decomposition of impregnated alkali metal salts results in a further increase in the basicity of these materials [3,4,7–11]. A significant contribution to the understanding of base catalysts involving supported alkali metal species has been achieved with these materials. However, the nature of the occluded alkali has been elusive,

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PII: S0920-5861(00)00425-9

and the actual form of the occluded oxide is still in question.

Zeolites containing alkali metals in the zeolite cages have also been investigated as high strength solid base catalysts. A novel preparation technique has been introduced in the literature in which alkali metal clusters are synthesized via the decomposition of alkali metal azides in the presence of a zeolite [12–20]. Decomposition of the occluded azide forms either ionic or neutral alkali metal clusters, depending primarily on the heating rate used to decompose the supported azide [19].

Over the last several years, we have derived important structure/function relationships for zeolite-supported base catalysts [21–23]. This paper summarizes our results from those characterization and reactivity studies and poses new questions to be addressed in future research.

2. Experimental

2.1. Catalyst synthesis

Ion-exchanged X and Y zeolites were prepared by triply ion-exchanging NaX (Union Carbide, lot No. 943191060078) and NaY (Union Carbide, lot No. 955089001010-S) with 1 M aqueous solutions of potassium nitrate or cesium acetate (Aldrich, 99.9%). Typically, the ion-exchange capacity of the zeolites is much lower for Cs than for K. For example, elemental analysis revealed that the extent of ion exchange in NaX was about 93% for K but only about 60% for Cs [21].

Zeolites containing occluded oxide clusters are referred to as CsO_x/CsX and CsO_x/CsY. These were obtained by incipient wetness impregnation of the cesium-exchanged zeolites with aqueous solutions of cesium acetate of the appropriate concentration. The impregnated catalysts were dried overnight in air at 373 K and calcined in flowing air at 773 K for 5 h. Since Cs-exchanged zeolites contain a significant fraction of Na that could not be removed by ion exchange, it is possible that high temperature treatment of zeolites containing occluded cesium acetate could facilitate solid state exchange resulting in formation of occluded sodium oxide. The extent of this solid state exchange process has not yet been evaluated. Nevertheless, samples prepared by impregnation and decomposition of cesium acetate will be referred to as zeolites containing occluded cesium oxide.

Zeolites containing occluded alkali metal clusters are referred to as Alkali/Alkali-X and Alkali/Alkali-Y, where “Alkali” stands for Na or Cs. The ion-exchanged zeolites were stirred in a solution of alkali azide (NaN_3: 99%, or CsN_3: 80–90 wt.% in methanol, Acros) in excess methanol at room temperature until the methanol evaporated. These catalysts were pretreated in situ before adsorption or catalytic experiments in order to decompose the azide and obtain the supported alkali metal. The presence of alkali metals in zeolites, after decomposition of the impregnated alkali azides, was confirmed by ESR spectroscopy [22].

Analysis by XPS provided insights into the distribution of alkali species on the zeolite samples [23]. The Cs/Si ratios for CsX, CsO_x/CsX (16 occluded Cs atoms/unit cell) and Cs/CsX obtained from XPS analysis, ranged from 0.43 to 0.46 indicating negligible surface enrichment of Cs for CsO_x/CsX and Cs/CsX. For comparison, the Cs/Si ratio for CsX obtained from bulk elemental analysis was 0.36. Thus, the “CsO_x” and Cs metal species in the as-synthesized samples appear to be well dispersed in the zeolite cages.

2.2. Adsorption methods

Iodine adsorption was performed in a U-shaped quartz tube with a quartz frit to support the sample. The mass of iodine adsorbed onto the sample was determined gravimetrically. Diffuse reflectance UV–visible spectra were recorded on a Varian Cary 13E spectrophotometer equipped with a Labsphere integrating sphere (DRA-CA-30) with a Labsphere spectralon reflectance standard (USRS-99-020). A complete description of the experimental procedures can be found elsewhere [21].

The energetics of the adsorption sites of alkali-modified zeolites were obtained via microcalorimetry of carbon dioxide adsorption. The microcalorimeter apparatus used in these experiments has been described elsewhere [24]. The alkali-exchanged and CsO_x-occluded zeolites were pretreated at 773 K for 5 h under vacuum, prior to carbon dioxide adsorption. All of the adsorption experiments were conducted isothermally at 373 K.

2.3. Catalytic probe reactions

Reaction of ethylene oxide with carbon dioxide to make ethylene carbonate was performed in a 50 ml high pressure batch reactor supplied by Parr Instrument. About 150 mg of catalyst were loaded into the reactor, after which a measured liquid volume of ethylene oxide was introduced to the reactor. The vessel was pressurized with carbon dioxide and heated to 423 K with constant stirring of the reaction mixture. The initial pressure in the reactor was about 1500 psig. The reaction was stopped after 3 h and the reaction mixture was extracted in acetone after filtering out the catalyst.

Decomposition of 2-propanol was carried out in a quartz U-tube continuous-flow fixed-bed reactor at 563 K and atmospheric pressure. Reactant 2-propanol was pumped to the system to give a vapor stream consisting of a 1:9 molar ratio with the helium carrier gas. The selectivity is defined as the rate of acetone production divided by the overall rate of 2-propanol consumption.

Double-bond isomerization of 1-butene was carried out in a single pass quartz fixed bed reactor at 373 K and atmospheric pressure. The reactant stream consisted of He (BOC gases) and 1-butene (Aldrich, 99+%) in a molar ratio of 9:1.

Side-chain alkylation of toluene with ethylene was carried out in a single pass quartz fixed bed reactor at 523 K and atmospheric pressure. The azide samples were decomposed (at 673 K for NaN_3, and 873 K for CsN_3) in flowing He prior to the reaction. Liquid toluene was pumped at a rate of 0.5 ml min^{-1} and vaporized into a flowing stream of He and ethylene. The molar ratios of He to ethylene to toluene in the reactant stream were 16:10:1.

Side-chain alkenylation of liquid-phase *o*-xylene with 1,3-butadiene was carried out in a semi-batch reactor fitted with a condenser and loaded with about 0.5 g of size selected (+40/−60) fresh supported azide sample, which was subsequently decomposed at 773 K in flowing N_2 to form the active catalyst. The reaction was initiated by bubbling a dilute stream of 1,3-butadiene (Aldrich, 99+%) at a rate of about 1.8 cm^3 min^{-1} through the *o*-xylene/catalyst mixture in a 9:1 ratio of dinitrogen to 1,3-butadiene. By using such a dilute stream, oligomerization of butadiene was reduced. Liquid samples were taken periodically (about every 1.5 h) in order to monitor the progress of the reaction.

3. Results and discussion

3.1. Adsorption of I_2 and CO_2

The UV–visible absorption spectrum of iodine has been used recently to rank donor strength of the basic oxygens in various zeolites [25]. Choi et al. [25] have shown that a blue shift occurs in the visible spectrum of adsorbed iodine with increasing electropositivity of the alkali counter-ion from Li to K, as well as with increasing aluminum content in the zeolite framework. These observations are consistent with the ranking of zeolite basicity determined by infrared studies [26] and alcohol decomposition reactions [27]. This correlation has also been made for the blue shift in the UV–visible absorption band of an iodine donor–acceptor complex to its heat of formation for solvated molecules [28–30].

Fig. 1 compares the spectrum of zeolite KX containing adsorbed iodine to that of pure silica MCM-41 loaded with a similar amount of I_2. The absorption peak at 509 nm for I_2 in MCM-41 is close that of iodine in the gas phase (520 nm), indicating that I_2 is weakly perturbed by adsorption onto silica. In contrast, the significant blue shift of the absorption band associated with iodine adsorbed on KX zeolite reveals a strong donor–acceptor interaction for the zeolite–iodine adsorption complex. Cesium-exchanged X and Y zeolites have an absorption feature at almost the same wavelength as their corresponding potassium exchanged zeolites. A linear relationship between energy shift and partial negative charge on oxygen (calculated from the Sanderson electronegativity equalization principle) was observed for the alkali metal exchanged zeolites [21].

We have attempted to extend this technique to characterize supported alkali species in zeolite pores and on oxides [21]. However, the iodine appeared to irreversibly react on these strongly basic samples, possibly forming an adsorbed triiodide ion. The reactivity of iodine on strong bases limits the usefulness of this technique to characterization of weak to moderate solid bases. To characterize alkali oxides occluded in zeolites, which are fairly strong bases, we used carbon dioxide adsorption microcalorimetry.

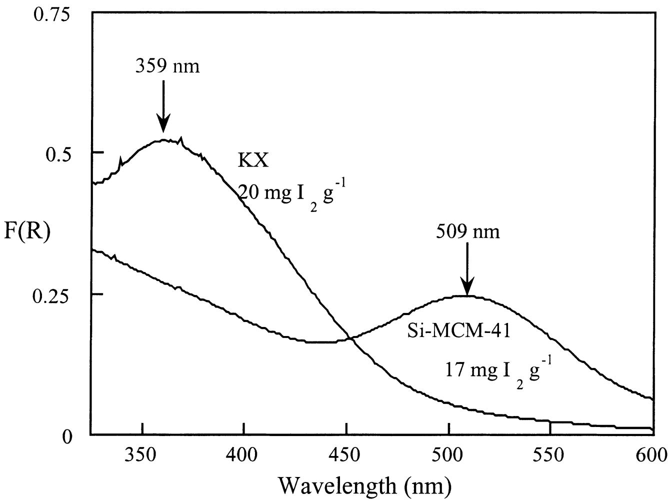

Fig. 1. UV–visible spectra of iodine adsorbed onto pure silica MCM-41 and KX zeolite at similar loading.

Fig. 2 compares the differential heat of CO_2 adsorption for Cs-exchanged Y zeolite with and without occluded cesium oxide. Thus, for the samples with occluded alkali metal oxide, there were a few sites with high heats of CO_2 adsorption (>100 kJ mol^{-1}). The adsorption energies decreased rapidly to a plateau, indicating that a majority of the sites had uniform strength. The strengths of a majority of the sites in CsO_x/CsY seemed to be unaffected by the CsO_x loading. Most of the adsorption sites in each of the CsO_x/CsY samples had energies close to 85 kJ mol^{-1}. Similar results were found for analogous X zeolites containing occluded cesium oxide [23]. The CO_2 uptakes on both X and Y zeolites indicate that about one CO_2 molecule was adsorbed for every four occluded Cs atoms, which suggests a very high dispersion of the occluded alkali.

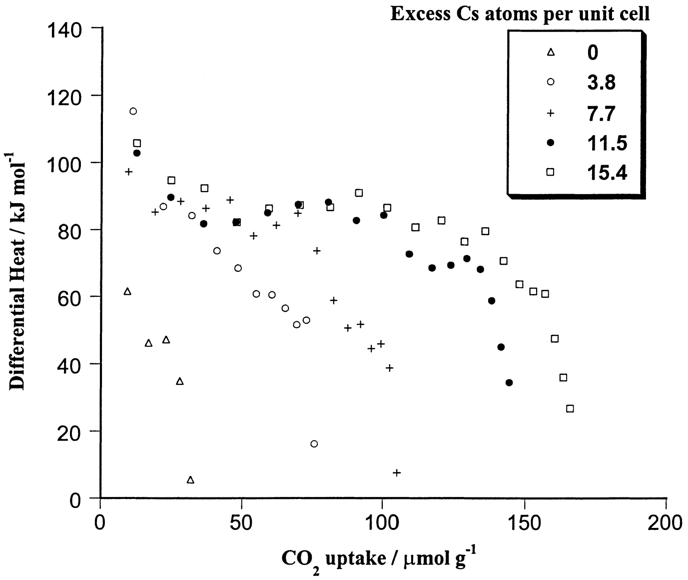

Fig. 2. Differential heats of adsorption as a function of carbon dioxide uptake for CsO_x/CsY zeolites.

As a reference for the cesium oxides occluded in zeolites, the enthalpy of CO_2 adsorption was measured at 373 K on bulk "Cs_2O" (Aldrich, 99+%) pretreated at 623 K for 5 h under vacuum [23]. The strongest sites on the bulk oxide had ΔH_{ads} of about 270 kJ mol^{-1}. Thus, the bulk oxide had significantly stronger sites than those in CsO_x/CsX and CsO_x/CsY. This difference in the adsorption energies of CsO_x clusters occluded in zeolites and the bulk "Cs_2O" compound indicates that the zeolite-occluded cesium species had a very different character than the bulk oxide.

3.2. Catalytic reactions

Alkali-exchanged zeolites were tested as catalysts for ethylene carbonate formation from ethylene oxide and carbon dioxide [21]. In all of the experiments, ethylene carbonate was the only product detected by gas chromatography. The activity of CsX for ethylene carbonate formation at 423 K showed a linear increase with time, reaching a yield of 31.6% after 10 h. For comparison purposes, the yield of ethylene carbonate after 3 h in a homogeneously catalyzed reaction using tetraethylammonium bromide was 76.3%. The yield of ethylene carbonate increased with increasing electropositivity of the exchange cation [21]. The rank of catalytic activities of the ion-exchanged X and Y zeolites compared very well to the expected order of basic strengths. Occlusion of cesium oxide in the X and Y zeolites improved activity for ethylene carbonate formation.

We have also studied the reaction of 2-propanol at 563 K on CsX zeolites containing occluded Cs oxide [22]. For CsX without any occluded cesium species located in the cages, the selectivity to acetone was 9%. The occlusion of CsO_x resulted in a significant increase in the selectivity due primarily to an increase in the rate of acetone production. For example, an order of magnitude increase in the loading of cesium oxide resulted in an analogous order of magnitude increase in the rate of acetone production over the range of Cs loadings presented.

A linear relationship was also seen between the rate of 1-butene isomerization and the number of occluded Cs atoms [23]. The turnover frequency at 373 K, based on excess Cs atoms, was calculated to be 2×10^{-3} s^{-1}. The high *cis*/*trans* ratio of the product 2-butenes (*cis*/*trans* = 19.1 over CsO_x/CsX containing 6.7 occluded Cs atoms per unit cell) indicated that the reaction occurred through a carbanion intermediate and hence was catalyzed by base sites. The *cis*/*trans* ratio for bulk "Cs_2O" was lower than that observed for most of the CsO_x/CsX zeolites, which supports our earlier argument that the nature of the occluded Cs species in CsO_x/CsX is different from a bulk "Cs_2O". However, it is not clear to us why the *cis*/*trans* ratio is lower on a catalyst with stronger base sites. Perhaps the small size of the supported oxide clusters and/or the zeolite pore structure affect selectivity for the butene reaction. Additional work is needed to clarify these results.

The zeolites containing alkali metals obtained by in situ decomposition of occluded alkali azides were characterized by ESR spectroscopy and tested as catalysts for alkylation and alkenylation reactions, specifically toluene alkylation with ethylene and *o*-xylene alkenylation with butadiene [22,23]. The samples containing occluded alkali metal oxides were inactive for these reactions.

The location of the central line *g*-value in the ESR spectrum of the alkali metal loaded KX zeolites indicated the formation of potassium clusters, despite using sodium and cesium azides as precursors [22]. This result was also reported by Xu and Kevan [13] for NaN_3 and CsN_3 decomposed on KX zeolite. Apparently, the zeolite cations exchanged with the impregnated alkali either during azide impregnation or thermal treatment. Reduction of potassium ions by cesium metal makes sense thermodynamically, but reduction of potassium ions by sodium metal is harder to rationalize. Perhaps the large amount of potassium in the zeolite ($K^+/NaN_3 = 5$) facilitates the transformation. Quantitative work clearly needs to be done in this area. Interestingly, both of the KX zeolites also exhibited broad ESR lines at high *g*-values, indicating the presence of additional extra-lattice alkali clusters.

Alkylation reactions yield very different product selectivities over acidic and basic catalysts. Usually, alkylation of aromatics over basic catalysts results in side-chain alkylation products, whereas over acidic catalysts ring alkylates are formed. Martens et al. [31] have studied the side-chain alkylation of alkylaromatics with ethylene over zeolites containing occluded alkali metals. They observed that the alkylation activity of Na metal in NaX zeolite was higher than that of Na metal in NaY zeolite.

Since exploratory tests with catalysts containing CsO_x did not reveal any products of the toluene alkylation reaction by GC analysis, we focused on the zeolites containing alkali metal. The metal-loaded X zeolites were active catalysts for the alkylation of toluene with ethylene at 523 K [23]. Side-chain alkylates were the only products detected by gas chromatography, which indicates the lack of residual acid sites on the catalysts. The selectivity of the reaction over Na/NaX, Na/CsX and Cs/CsX at 10–15% toluene conversion was greater than 95% to mono and di-alkylates. The alkali metals occluded in Y zeolites (Na/NaY and Cs/NaY) showed no activity for the reaction under our conditions.

Adsorption of O_2 onto Cs/CsX resulted in an order of magnitude decrease in activity for the alkylation reaction [23]. A similar result was obtained on Cs/CsX for the isomerization of 1-butene. However, after heating Cs/CsX to 773 K after O_2 adsorption, the catalyst recovered its activity for 1-butene isomerization, whereas a similar treatment eliminated completely the activity for the alkylation reaction. Even though alkali metal oxides are strong bases, they are not strong enough to catalyze the alkylation reaction.

We also investigated the liquid alkenylation reaction of *o*-xylene with butadiene to form 5-*o*-tolyl-2-pentene (OTP) [22]. Like toluene alkylation with ethylene, the alkenylation reaction requires a stronger base site than that associated with supported alkali oxides.

Ring alkenylation accounted for about 3% of the total mono-alkenylated product. The selectivity to OTP, based on the total amount of mono-, di- and tri-alkenylated products, was greater than 85% for *o*-xylene conversions ranging from 1 to 14%. The active materials were true catalysts since the ratio of the amount of *o*-xylene reacted to the theoretical amount of alkali metal present exceeded unity after a reaction time of 7.5 h. The OTP product formed over Cs/KX had a *trans*/*cis* ratio of 1:3, which was close to that seen over unsupported potassium metal, which according to ESR spectroscopy was present in the zeolite cages.

Extra-lattice metal clusters were evident on each of the alkali metal loaded zeolites that were effective catalysts for the alkenylation reaction, suggesting that these clusters might be the active species. For each reaction in which OTP was produced, the solution color indicated that alkali metal formed from the decomposition of the supported azide may have leached into solution to form an organoalkali complex. Thus catalytic activity was likely due to metal species in the solution as well as those associated with the zeolite (possibly through reaction with the zeolite). Nevertheless, the studies showed interesting ways to generate active alkali species for carrying out alkenylation.

4. Conclusions

The basicity of ion-exchanged zeolites was effectively ranked by the blue shift in the UV–visible spectrum of adsorbed iodine. However, incorporation of cesium oxide clusters in zeolite supercages created strong base sites that decomposed iodine. Carbon dioxide adsorption microcalorimetry proved to be a quantitative probe of the strong, extra-lattice, basic sites. Comparison of the differential heats of carbon dioxide adsorption suggests that bulk cesium oxide is a much stronger base than zeolite-supported cesium oxide. Very strong base sites can be prepared by decomposing alkali azides impregnated onto zeolites. A wide variety of catalytic reactions can be used to classify the basic materials synthesized in this work. Formation of ethylene carbonate from ethylene oxide and carbon dioxide was catalyzed by ion-exchanged zeolites, which are fairly weak bases. The decomposition of 2-propanol to acetone and the isomerization of 1-butene to *cis*-2-butene appear to require the presence of occluded alkali metal oxides. Alkylation of toluene with ethylene and alkenylation of *o*-xylene with butadiene require the presence of alkali metals on the zeolites, which are very strong bases. The combination of selective adsorption of probe molecules and application of appropriate catalytic reactions provides a consistent description of basic zeolites containing occluded alkali species.

Acknowledgements

This work was supported by the Department of Energy (Basic Energy Sciences, Grant DEFG05-95ER-14549).

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