1. Effect of postsynthesis preparation procedure on the state of copper in CuBEA zeolites and its catalytic properties in SCR of NO with NH3

By Baran, Rafal; Averseng, Frederic; Wierzbicki, Dominik; Chalupka, Karolina; Krafft, Jean-Marc; Grzybek, Teresa; Dzwigaj, Stanislaw
From Applied Catalysis, A: General (2016), 523, 332-342. Language: English, Database: CAPLUS, DOI:10.1016/j.apcata.2016.06.008

Cu-contg. BEA zeolites, $Cu_{2.0}$SiBEA and $Cu_{2.0}$HAlBEA, with 2% of Cu were prepd. by a 2-step post-synthesis method and a conventional wet impregnation, resp. These zeolites were characterized by XRD, DR UV-visible, EPR, FTIR and TPR physicochem. techniques. The incorporation of Cu into framework of SiBEA was evidenced by XRD. The state of Cu in both zeolites was studied by DR UV-visible and EPR. The acidity of $Cu_{2.0}$SiBEA and $Cu_{2.0}$HAlBEA was detd. by FTIR of adsorbed CO and pyridine. The reducibility of the Cu species present in both zeolites was studied by TPR and their catalytic properties were studied in selective catalytic redn. of NO with NH_3. Both $Cu_{2.0}$SiBEA and $Cu_{2.0}$HAlBEA zeolite catalysts showed very high activity in this reaction with the NO conversion >80% and N_2 selectivity >95% at 473-623 K. The higher NO conversion and N_2 selectivity in SCR of NO with NH_3 at the high temp. range for the $Cu_{2.0}$HAlBEA than for $Cu_{2.0}$SiBEA suggest that the strong Broensted and Lewis acidic sites related to the framework and extra-framework Al atoms play an important role in SCR of NO process.

~3 Citings

2. Investigating the DMPO-formate spin trapping method for the study of paper iron gall ink corrosion

By Gimat, Alice; Kasneryk, Valeryia; Dupont, Anne-Laurence; Paris, Sabrina; Averseng, Frederic; Fournier, Jeanine; Massiani, Pascale; Rouchon, Veronique
From New Journal of Chemistry (2016), 40(11), 9098-9110. Language: English, Database: CAPLUS, DOI:10.1039/C6NJ01480A

Paper degrdn. by iron gall ink is a challenging issue for the conservation of ancient manuscripts. It is usually attributed to both Fe^{II} catalyzed oxidn. and acid catalyzed hydrolysis of cellulose, yet the dominant degrdn. pathway remains an open question. In this work, ESR spectroscopy (ESR) was used to identify radicals involved in cellulose degrdn. Papers impregnated with iron salts were put in contact with an aq. soln. of DMPO (spin-trap) and analyzed by ESR. No DMPO-OH adducts were detected while the addn. of formate, an intermediary target mol., led on the contrary to the detection of a significant amt. of DMPO-$CO_2{}^{-}$ adducts. This reveals the predominant occurrence of reactive oxygen species (ROS) other than hydroxyl radicals (most likely superoxide or hydroperoxyl radicals). The prodn. of DMPO-$CO_2{}^{-}$ adducts was found to be oxygen dependent and to originate mainly from ferrous ions lixiviated from the impregnated papers. At high iron loads (above 1 mmol L^{-1}), it was shown that quantification of these adducts should be done with great care because of a competing formation of hydroxylamine that jeopardizes the ESR signal. Complementary TPA hydroxylation measurements performed by HPLC on ink and iron sulfate impregnated papers revealed some prodn. of hydroxyl radicals but at a concn. several orders of magnitude below that of the ROS detected with formation of DMPO-$CO_2{}^{-}$ adducts. This HO prodn. was moreover not correlated with cellulose chain scissions, indicating that autoxidn. by these radicals is not the main mechanism of cellulose depolymn. in presence of iron gall ink.

~1 Citing

3. Molecular Understanding of the Bulk Composition of Crystalline Nonstoichiometric Hydroxyapatites: Application to the Rationalization of Structure-Reactivity Relationships

By Ben Osman, Manel; Krafft, Jean Marc; Millot, Yannick; Averseng, Frederic; Yoshioka, Tetsuya; Kubo, Jun; Costentin, Guylene
From European Journal of Inorganic Chemistry (2016), 2016(17), 2709-2720. Language: English, Database: CAPLUS, DOI:10.1002/ejic.201600244

Cryst. hydroxyapatite samples (HAps) have been prepd. by using the co-pptn. method under various pH conditions, leading to nonstoichiometric solids (1.65 < Ca/P < 1.77). The aim of this study was to rationalize the sensitivity of the catalytic activity of HAps to their bulk compns. going from the macroscopic level expressed by the Ca/P ratio to the mol. level properties of the bulk. From DRIFT, ^{31}P NMR and Raman characterizations, hydroxyapatites were obtained with a range of structural defects compared with the ideal stoichiometric compd. If the amt. of $HPO_4{}^{2-}$ and B-type carbonates directly impacts the Ca/P ratio, it is not the case for A-type carbonates. All these defects, and esp. the A-type carbonates, participate in the modulation of OH content inside the channels. Irresp. of the Ca/P values, the OH concn. appears to be perfectly related to the surface basic reactivity measured through 2-methyl-3-butyn-2-ol (MBOH) conversion. Thus, except for the similar carbonate content (in cases of low Ca/P values), the Ca/P ratio is not sufficient to predict the catalytic behavior of all HAps synthesized under various conditions: in the case of variable carbonate content monitored under different pH conditions, a larger range of Ca/P ratio can be obtained including over-stoichiometric HAps samples (Ca/P > 1.67), and the bulk OH concn. becomes a much better descriptor than the Ca/P ratio to account for the basic reactivity.

~2 Citings

4. Controlled introduction of nickel in the BEA zeolite by post-synthesis methods

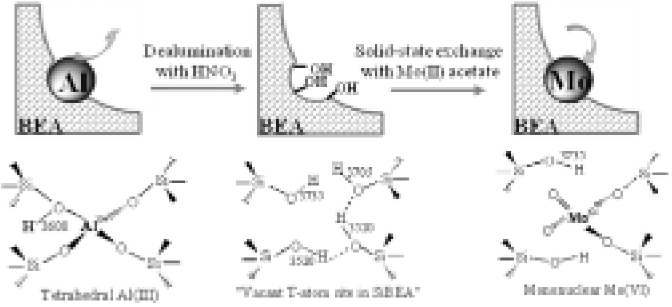
By Tesler, Larry; Dzwigaj, Stanislaw; Averseng, Frederic
From Abstracts of Papers, 247th ACS National Meeting & Exposition, Dallas, TX, United States, March 16-20, 2014 (2014), INOR-602. Language: English, Database: CAPLUS

The oxidn. state, dispersion and environment of transition metals present in catalysts play an important role in their catalytic properties and stability. Hence, one must control each step of catalyst prepn. in order to obtain the desired final material. Our work focused on the prepn. of $Ni_xHAlBEA$ and Ni_xSiBEA zeolites (x = 0.5 - 7.0 wt. $Ni_xHAlBEA$ were prepd. by conventional wet impregnation and Ni_xSiBEA by a two-step postsynthesis procedure, which consisted of dealumination of BEA zeolite with nitric acid (13 mol L^{-1}) and formation, in resulted SiBEA, of vacant T-atom sites with assocd. silanol groups and then incorporation of nickel ions into vacant T-atom sites by reaction with silanol groups [1]. XRD, DR UV-vis and XPS evidenced that nickel ions are present in the framework of calcined Ni_xSiBEA as pseudo-tetrahedral Ni(II), identified by the DR UV-vis bands between 450 - 643 nm (Fig. 1), while they are mainly in extra-framework position of calcined $Ni_xHAlBEA$. The redn. of both C-Ni_xSiBEA and C-$Ni_xHAlBEA$ leads to the formation of square-planar extra-framework Ni(I) species and Ni(0) nanoparticles as showed by EPR. DR UV-Vis spectra of as-prepd., calcined (C-), and rehydrated (reh-C-) $Ni_{1.0}SiBEA$.[1] A. Penkova, S. Dzwigaj, R. Kefirov, K. Hadjiivanov, M. C 2007 , 111, 8623.

~0 Citings

5. Incorporation of Mo into the Vacant T-Atom Sites of the Framework of BEA Zeolite as Mononuclear Mo Evidenced by XRD and FTIR, NMR, EPR, and DR UV-Vis Spectroscopies

By Baran, Rafal; Averseng, Frederic; Millot, Yannick; Onfroy, Thomas; Casale, Sandra; Dzwigaj, Stanislaw
From Journal of Physical Chemistry C (2014), 118(8), 4143-4150. Language: English, Database: CAPLUS, DOI:10.1021/jp410016g



A MoSiBEA zeolite was prepd. by a two-step post-synthesis procedure that consists of 1st creating the vacant T-atom sites with assocd. silanol groups by treatment of TEABEA zeolite with nitric acid and then incorporating Mo ions into the vacant T-atom sites by solid-state ion exchange at 773 K using molybdenum(II) acetate. The incorporation of Mo ions into the vacant T-atom sites of the framework of SiBEA zeolite as isolated mononuclear Mo(VI) species was evidenced by the combined use of XRD and FTIR, NMR, and diffuse reflectance UV-visible spectroscopies. The consumption of OH groups was monitored by FTIR spectroscopy. The reducibility of Mo was studied by TPR and EPR spectroscopy. The size of very small well-dispersed Mo(0) nanoparticles formed upon treatment of MoSiBEA between 298 and 1240 K in hydrogen stream (5% H_2/Ar) was measured by TEM.

~11 Citings

6. An unstable paramagnetic isopolyoxomolybdate intermediate non-homogeneously reduced at different sites and trapped in a host based on chemical adaptability

By Merca Alice; Garai Somenath; Bogge Hartmut; Haupt Erhard T K; Ghosh Amrita; Lopez Xavier; Poblet Josep M; Averseng Frederic; Che Michel; Muller Achim
From Angewandte Chemie (International ed. in English) (2013), 52(45), 11765-9, Language: English, Database: MEDLINE

~1 Citing

7. An Unstable Paramagnetic Isopolyoxomolybdate Intermediate Non-Homogeneously Reduced at Different Sites and Trapped in a Host Based on Chemical Adaptability

By Merca, Alice; Garai, Somenath; Boegge, Hartmut; Haupt, Erhard T. K.; Ghosh, Amrita; Lopez, Xavier; Poblet, Josep M.; Averseng, Frederic; Che, Michel; Mueller, Achim
From Angewandte Chemie, International Edition (2013), 52(45), 11765-11769. Language: English, Database: CAPLUS, DOI:10.1002/anie.201305402

A metal oxide host with a trapped unstable {Mo36}-type polyoxomolybdate guest exhibits independent reduced diamagnetic building blocks and paramagnetic centers. The guest in such systems is stabilized esp. by a hydrogen-bond network between the core and the shell.

~7 Citings

8. Mononuclear pseudo-tetrahedral V species of VSiBEA zeolite as the active sites of the selective oxidative dehydrogenation of propane

By Chalupka, Karolina; Thomas, Cyril; Millot, Yannick; Averseng, Frederic; Dzwigaj, Stanislaw
From Journal of Catalysis (2013), 305, 46-55. Language: English, Database: CAPLUS, DOI:10.1016/j.jcat.2013.04.020

This work reports on the study of the influence of the nature of the V species in the ODH of propane. For this purpose, VSiBEA catalysts, including framework and/or extra-framework V species, were synthesized via the 2-step method by controlling the speciation of the V species of the aq. NH_4VO_3 solns. (via the pH of the corresponding solns.) to which the SiBEA zeolite was contacted with. The samples were characterized by N_2 physisorption, XRD, FTIR, ^{27}Al, ^{29}Si and ^{57}V NMR, DR UV-visible and EPR. The TOF of the C_3H_8 ODH reaction of the samples exhibiting framework V species are in good agreement with those reported in earlier works for which V species were highly dispersed on various SiO_2 supports and 1 order of magnitude higher than those of the samples exhibiting extra-framework V species, suggesting that isolated pseudo-tetrahedral framework V species would be the active sites of the C_3H_8 ODH catalytic reaction. EPR measurements of the spent catalysts indicated that these pseudo-tetrahedral framework V species were stable under the C_3H_8 ODH reaction conditions and were much more abundant in the $V_{0.70}$SiBEA sample (for which incorporation of V in the SiBEA framework was targeted) than in the $V_{1.00}$SiBEA sample (for which deposition of V occurred both in framework and extra-framework positions of SiBEA).

~12 Citings

9. Origins of the deactivation process in the conversion of methylbutynol on zinc oxide monitored by operando DRIFTS

By Drouilly, Charlotte; Krafft, Jean-Marc; Averseng, Frederic; Lauron-Pernot, Helene; Bazer-Bachi, Delphine; Chizallet, Celine; Lecocq, Vincent; Costentin, Guylene
From Catalysis Today (2013), 205, 67-75. Language: English, Database: CAPLUS, DOI:10.1016/j.cattod.2012.08.011

The catalytic behavior of zinc oxide samples was studied thanks to a model methylbutynol (MBOH) conversion reaction. The formation of acetone and acetylene is indicative of the basic properties of the zinc oxide surface. This basic catalyst, whose conversion level depends on the nature of the pre-treatment, was found to deactivate vs. time on stream. Poisoning the basic sites by CO_2 pre-adsorption only affects the active sites working at the beginning of the reaction, those still working at steady state being not impacted. This is consistent with the modification of the strength and population of the active sites during the catalytic reaction. Indeed, from operando DRIFTS expts., at the beginning of the reaction, the strong acid base pairs generated upon inert treatment at 773 K promote the self aldol condensation of acetone, leading to oligomers. This reaction also produces water, which dissocs. on the surface, filling up oxygen vacancies. This contributes to the lowering of the strength of the active sites, resulting in the quenching of polymn. of acetone at a certain stage, at the benefit of the increase of the amt. of diacetone alc. Consistently, pre-adsorption of water was shown to lead to a decrease of the conversion level, resulting in a conversion profile similar to that obtained after 10 min of reaction in the absence of pre-adsorbed water. The poisoning mechanism proposed is based on the evolution of the IR bands vs. time and is in line with the evolution of the deactivation profile vs. time. It is concluded that both the control of the conversion level and the dependence of the reaction toward deactivation are assocd. to the formation of oxygen vacancies during the pre-treatment step but also on their stability in the conditions on the implemented catalytic reaction.

~4 Citings

10. Role of oxygen vacancies in the basicity of ZnO: From the model methylbutynol conversion to the ethanol transformation application

By Drouilly, Charlotte; Krafft, Jean-Marc; Averseng, Frederic; Lauron-Pernot, Helene; Bazer-Bachi, Delphine; Chizallet, Celine; Lecocq, Vincent; Costentin, Guylene
From Applied Catalysis, A: General (2013), 453, 121-129. Language: English, Database: CAPLUS, DOI:10.1016/j.apcata.2012.11.045

The parameters governing the basic reactivity of kadox and ex-carbonate zinc oxide samples towards alc. conversion were investigated varying the atm. of pre-treatment for a model reaction, the methylbutynol (MBOH) conversion, and the ethanol conversion reaction, a transformation of potential higher industrial impact. The catalytic properties of ZnO can thus be tuned: enhanced activities were measured after a pre-treatment performed under inert gas as compared to oxidative conditions. If no significant variation of residual hydroxylation nor carbonation can account for this behavior, a quant. correlation between the variation of MBOH conversion induced by the different atm. of pre-treatment with that of the concn. in oxygen vacancies characterized by in situ EPR found, showing that oxygen vacancies play a key role towards basic reactivity. In fact, the electronic d. of the oxygen of the active acid/base pair is directly influenced by the electron release or capture assocd. to the formation or filling up of oxygen vacancies, resp. On the kadox samples, the presence of an addnl. weaker active site is responsible for the residual activity of kadox sample in the absence of oxygen vacancies. The existence and location on specific crystallog. faces of these sites are discussed in relation with the different morphologies of the two samples and with their different affinity with CO_2. Even if the occurrence of oxygen vacancies still governs the conversion level for ethanol transformation, the reactivity inhibition after oxidative pre-treatment is less pronounced due to the higher reaction temp. that limits the efficiency of oxygen vacancies filling-up under oxidative atmospheres. The nature of active sites leading to the formation of acetaldehyde and ethylene is also discussed.

~12 Citings

11. Understanding of the oxygen activation on ceria- and ceria/alumina-supported gold catalysts: a study combining 18O/16O isotopic exchange and EPR spectroscopy

By Lakshmanan, Pandian; Averseng, Frederic; Bion, Nicolas; Delannoy, Laurent; Tatibouet, Jean-Michel; Louis, Catherine
From Gold Bulletin (Berlin, Germany) (2013), 46(4), 233-242, 10 pp.. Language: English, Database: CAPLUS, DOI:10.1007/s13404-013-0103-z

Gold supported on ceria or ceria-alumina mixed oxides are very active catalysts for total oxidn. of a variety of mols. The key step of the oxygen activation on such catalysts is still a matter of debate. Gold-ceria (Au/CeO2) and gold-ceria-alumina (Au/CeO2/Al2O3) catalysts were prepd. by deposition-pptn. of gold precursor with urea as in former works where their efficiency to catalyze the oxidn. of propene and propan-2-ol was demonstrated. To understand the phenomenon of oxygen activation over this class of catalysts, efficient techniques generally used to characterize the interaction between oxygen and cerium-based oxides were applied; the oxygen storage capacity (OSC) measurement, the 18O2/16O2 isotopic exchange study (OIE), as well as characterizations by in situ Raman and ESR (EPR) spectroscopies. Each of the techniques allowed showing the impact of the gold nanoparticles on the activation of dioxygen, on the kinetic governing the gas-phase/solid oxygen atom exchange, and on the nature and the location of the adsorbed oxygen species. Gold nanoparticles were shown to increase drastically the OSC values and the rate of oxygen exchange. OIE study demonstrated the absence of pure equilibration reaction (16O2(g) + 18O2(g) ↔ 2 16O18O(g)), indicating that gold did not promote the dissocn. of dioxygen. Peroxo adspecies were obsd. by Raman spectroscopy only in the presence of gold. On the contrary, EPR spectroscopy indicated that the concn. of superoxo adspecies was lower for oxide-supported gold samples than for bare oxides. The combination of techniques allowed reinforcing the hypothesis that the gold nanoparticules promote the activation of dioxygen by generating extremely mobile diat.-oxygenated species at the gold/ceria interfacial perimeter. This specific gold-ceria interaction, which leads to the increase in oxygen mobility, is probably also responsible for the higher catalytic performance of Au/CeO2 and Au/CeO2/Al2O3 in oxidn. reaction compared to bare supports.

~2 Citings

12. Influence of the preparation procedure on the nature and environment of vanadium in VSiBEA zeolite: XRD, DR UV-vis, NMR, EPR and TPR studies

By Baran, Rafal; Millot, Yannick; Onfroy, Thomas; Averseng, Frederic; Krafft, Jean-Marc; Dzwigaj, Stanislaw
From Microporous and Mesoporous Materials (2012), 161, 179-186. Language: English, Database: CAPLUS, DOI:10.1016/j.micromeso.2012.05.023

Two series of V_xSiBEA(I) and V_xSiBEA(II) zeolites have been prepd. by a two-steps postsynthesis method which consists, in the first step, in the dealumination of TEABEA zeolite by two different procedures to obtain SiBEA(I) and SiBEA(II) zeolites and then, in the second step, in contacting the obtained zeolites with an aq. NH_4VO_3 soln. at pH 2.7. Because the NH_4VO_3 soln. at pH 2.7 predominantly contains mononuclear $VO_2{}^+$ ions, vanadium can be incorporated into SiBEA(I) and SiBEA(II) as framework pseudo-tetrahedral non hydroxylated $(SiO)_3V(V)=O$ and hydroxylated $(SiO)_2(OH)V(V)=O$ species by reaction with silanol groups of vacant T-atom sites. Combined use of FTIR, DR UV-vis, ^{51}V NMR, EPR and TPR allows to det. the oxidn. state, nature and environment of vanadium in as prepd., calcined, rehydrated, activated and reduced V_xSiBEA(I) and V_xSiBEA(II) samples. It is shown that the procedure of dealumination has the effect on the properties of the silanol groups of vacant T-atom sites in SiBEA(I) and SiBEA(II) and on the nature and environment of V species in as prepd. V_xSiBEA(I) and V_xSiBEA(II). As evidenced by DR UV-vis and ^{51}V MAS NMR in V_xSiBEA(II), vanadium is present only as pseudo-tetrahedral V(V) species, and in contrast in V_xSiBEA(I) as pseudo-tetrahedral and octahedral V(V) species. The oxidn. state of framework tetrahedral vanadium in V_xSiBEA(I) and V_xSiBEA(II) easily change upon calcination in oxygen, outgassing at 773 K and reducing with hydrogen at high temp. (873 K), as shown by EPR. The presence of Bronsted and Lewis acidic centers are evidenced in V_xSiBEA(II) by FTIR adsorption investigations of pyridine and CO used as probe mols.

~9 Citings

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13. Substituent effects on the spin-transition temperature in complexes with tris(pyrazolyl) ligands

By Paulsen, Hauke; Duelund, Lars; Zimmermann, Axel; Averseng, Frederic; Gerdan, Michael; Winkler, Heiner; Toftlund, Hans; Trautwein, Alfred X.
From arXiv.org, e-Print Archive, Physics (2012), 1-12, arXiv:1206.1883v1 [physics.chem-ph]. Language: English, Database: CAPLUS, DOI:10.1007/s00706-002-0522-7

Iron(II) complexes with substituted tris(pyrazolyl) ligands, which exhibit a thermally driven transition from a low-spin state at low temps. to a high-spin state at elevated temps., have been studied by Mossbauer spectroscopy and magnetic susceptibility measurements. From the obsd. spectra the molar high-spin fraction and the transition temp. have been extd. All substituents, except for bromine, decreases the transition temp. D. functional calcns. have been carried out to compare the exptl. obsd. shifts of the transition temp. with those derived from theory.

~0 Citings

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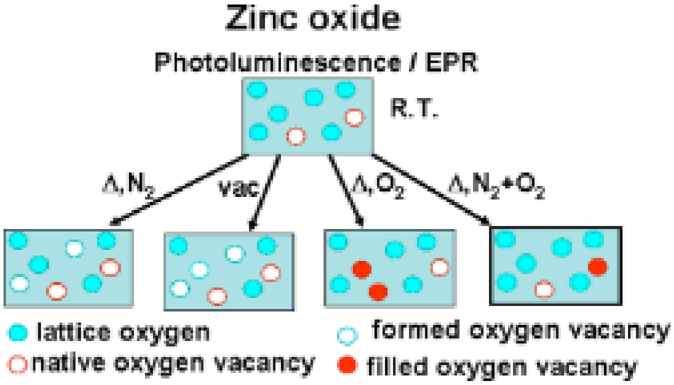
14. ZnO Oxygen Vacancies Formation and Filling Followed by in Situ Photoluminescence and in Situ EPR

By Drouilly, Charlotte; Krafft, Jean-Marc; Averseng, Frederic; Casale, Sandra; Bazer-Bachi, Delphine; Chizallet, Celine; Lecocq, Vincent; Vezin, Herve; Lauron-Pernot, Helene; Costentin, Guylene
From Journal of Physical Chemistry C (2012), 116(40), 21297-21307. Language: English, Database: CAPLUS, DOI:10.1021/jp307693y



O vacancies of ZnO were followed by luminescence (PL) and ESR spectra. The green PL emission was assocd. with O vacancies: its intensity is enhanced upon static thermal treatment under inert or under vacuum, whereas it decreases upon O treatment. A unique ESR signal at g = 1.96 was measured at room temp. after thermal in situ treatment under flow of inert or oxygenated atms., its double integration follows the same trends than the green PL emission and its evolution was shown to probe the O vacancy concns. The relative concn. of the related paramagnetic species would be increased/decreased upon trapping/release of the electron assocd. to the formation/filling of O vacancy. The influence of Ti impurities on the PL and ESR signals was studied. The ESR signal is related to O vacancies and its position shift could be explained by the involvement of some mixing orbitals. Thanks to static (PL and EPR) and dynamic (EPR) in situ characterizations, the conditions of formation or filling of O vacancies are discussed depending of the atm. and temp. of the pretreatment of kadox and ex-carbonate Zn oxide. High temp. treatments, inert atms., and vacuum give new O vacancies. This process is reversible upon oxygenated atms. The efficiency of such filling up depends on the temp. and starts to prevail on the O vacancy formation <500 K. Few native O vacancies can also be filled up.

~41 Citings

15. Effect of iron impurities on the catalytic activity of BEA, MOR and MFI zeolites in the SCR of NO by ethanol

By Dzwigaj, Stanislaw; Janas, Janusz; Rojek, Wojciech; Stievano, Lorenzo; Wagner, Friedrich E.; Averseng, Frederic; Che, Michel
From Applied Catalysis, B: Environmental (2009), 86(1-2), 45-52. Language: English, Database: CAPLUS, DOI:10.1016/j.apcatb.2008.07.017

The combined use of chem. anal., x-ray diffraction, ESR, and Moessbauer techniques provided detailed information on the nature of Fe impurities in com. BEA, MOR, and MFI zeolites. EPR and Moessbauer spectroscopies showed Fe impurities occur mainly as tetrahedral Fe^{3+} species and to a minor extent as octahedral Fe^{3+} species; relative amts. depend on zeolite type. Fe impurities present in com. BEA, MOR, and MFI zeolites are active in the selective catalytic redn. (SCR) of NO by ethanol, with NO conversion >37, >43 and >50% for BEA, MOR and MFI, resp., and with selectivity toward N_2 >90% for all zeolites at 575-775° K. The much higher activity of com. BEA, MOR, and MFI than FeSiBEA and CoSiBEA, both prepd. by a 2-step post-synthesis method, suggested Fe^{3+} impurities in com. zeolites occur in tetrahedral and/or octahedral environments, possibly close to lattice Al, making them active in the SCR of NO by ethanol. Bronsted and Lewis acidic sites in studied zeolites were detd. by Fourier transform IR spectroscopy measurements of pyridine adsorption.

~11 Citings

16. Remarkable effect of the preparation method on the state of vanadium in BEA zeolite: Lattice and extra-lattice V species

By Dzwigaj, S.; Ivanova, E.; Kefirov, R.; Hadjiivanov, K.; Averseng, F.; Krafft, J. M.; Che, M.
From Catalysis Today (2009), 142(3-4), 185-191. Language: English, Database: CAPLUS, DOI:10.1016/j.cattod.2008.09.031

The state of vanadium in two BEA zeolites is investigated by XRD, FTIR, DR UV-vis and EPR. One of the samples, VAlBEA (1.3 wt.% of V), is prepd. by conventional ion exchange and the other, VSiBEA (2.0 wt.% of V), by a two-step postsynthesis method involving dealuminated BEA zeolite. No structural changes are obsd. after incorporation of vanadium into AlBEA zeolite by ion-exchange method. In contrast, the impregnation of SiBEA with V(IV) ($VOSO_4$) precursor leads to an increase of unit cell parameters of the BEA, to the consumption of silanol groups in vacant T-sites and incorporation of V in the framework of BEA zeolite as well dispersed tetrahedral V(V) species. NO and CO used as IR probe mols., DR UV-vis and EPR allow to establish the oxidn. state of vanadium in as prepd., oxidized, activated and reduced VAlBEA and VSiBEA zeolites. The IR spectra of oxidized, activated and reduced VAlBEA samples are very similar. It suggests that V introduced by ion exchange in extra-lattice position is stabilized on all samples in similar oxidn. state. CO adsorption evidence the presence of vanadium in IV oxidn. state via IR bands at about 2200 and 2180 cm^{-1} assigned to V(IV)-CO monocarbonyl and V(IV)-$(CO)_2$ dicarbonyl species. In contrast, the oxidn. state of V in VSiBEA changes strongly in function of calcinations in oxygen, outgassing at high temp. (773 K) and reducing with hydrogen at high temp. (873 K). This shows that lattice tetrahedral V species change easily oxidn. state and this property allows them to be good candidate as active site of selective redox reactions.

~13 Citings

17. Grafting and anchoring of transition metal complexes to inorganic oxides

By Averseng, Frederic; Vennat, Maxence; Che, Michel
Edited By:Ertl, Gerhard
From Handbook of Heterogeneous Catalysis (2nd Edition) (2008), 1, 522-539. Language: English, Database: CAPLUS

A review; grafting and anchoring of transition metal complexes to inorg. oxides for heterogeneous catalysts is discussed.

~12 Citings

18. A two-step spin transition and order-disorder phenomena in the mononuclear compound [Fe(Hpy-DAPP)](BF4)2

By Matouzenko, Galina S.; Luneau, Dominique; Molnar, Gabor; Ould-Moussa, Nawell; Zein, Samir; Borshch, Serguei A.; Boussekso u, Azzedine; Averseng, Frederic
From European Journal of Inorganic Chemistry (2006), (13), 2671-2682. Language: English, Database: CAPLUS, DOI:10.1002/ejic.200600068

This paper reports the synthesis and detailed characterization of mononuclear $[Fe^{II}(Hpy\text{-}DAPP)](BF_4)_2$(Hpy-DAPP = {bis[N-(2-pyridylmethyl)-3-aminopropyl](2-pyridylmethyl)amine}), which manifests a two-step spin crossover accompanied by an ordering and a conformational transition in the ligand. The magnetic susceptibility measurements and Mossbauer spectra reveal that the two steps of the spin transition are sepd. by an inflection point at ~130 K at which 50% of the complex undergoes a spin conversion. The high-temp. step centered at 181 K is gradual, whereas the low-temp. one displays a thermal hysteresis with two transition temps. ($T_{c\downarrow}$ = 119 and $T_c\uparrow$ = 123 K). The single-crystal x-ray structure was detd. for the HS (298 K) and LS (90 K) forms, as well as for the mixed form with an HS:LS ratio of 1:1 (130 K). The structural studies show that the crystal lattice contains a single Fe^{II} crystallog. site over the whole temp. range. At room temp., the most important peculiarity of the HS complex structure is the disorder of the N3 amino aliph. atom, which is in the 1st coordination sphere of Fe^{II}, over two positions. The strong involvement of the N3 atoms in H-bonding with two neighboring counterions is considered as a possible origin of this disorder. At 130 K, the disorder is increased by the distribution of the N1 and C9 atoms over two positions, leading to the conformational disorder (chair and twist-boat conformations with a 1:1 ratio) in the six-membered N2C7C8C9N1Fe chelate cycle. At 90 K, the disorder in the positions of the N1, N3, and C9 atoms disappears and the N2C7C8C9N1Fe metallacycle adopts a unique twist-boat conformation. The results of structural studies suggest that the two-step spin-transition behavior of $[Fe(Hpy\text{-}DAPP)](BF_4)_2$ is induced by two different geometries of the $[FeN_6]$ coordination core generated by the disorder in the ligand. The HS → LS transition is also assocd. with the conformational change in the chelate cycle. Both crystallog. data anal. and electronic structure calcns. allow the authors to relate the disordered geometries of the $[FeN_6]$ coordination core to their HS and LS character.

~33 Citings

19. Synthesis, crystal structures, and molecular hyperpolarizabilities of a new Schiff base ligand, and its copper(II), nickel(II), and cobalt(II) metal complexes

By Lacroix, Pascal G.; Averseng, Frederic; Malfant, Isabelle; Nakatani, Keitaro
From Inorganica Chimica Acta (2004), 357(13), 3825-3835. Language: English, Database: CAPLUS, DOI:10.1016/j.ica.2004.03.004

A new ligand (HL) obtained from the Schiff base condensation of 4-(diethylamino)salicylaldehyde with 4-nitroaniline is reported along with its nickel(II), copper(II), and cobalt(II) complexes. The crystal structures are reported for the four compds. While $Ni^{II}L_2$ and $Cu^{II}L_2$ are centrosym. mols., $Co^{II}L_2$ exhibits a pseudo-tetrahedral mol. structure. The quadratic hyperpolarizabilities (β) of HL and $Co^{II}L_2$, measured by elec. field induced 2nd harmonic (EFISH) technique, are equal to 66 and 110 × 10^{-30} cm^5 esu^{-1}, resp. Beside a geometric effect (pseudo-T_d symmetry), the coordination of the metal center provides an intrinsic enhancement of the NLO response. An enhancement of the thermal stability of ~60° is found upon metal complexation.

~59 Citings

20. Substituent effects on the spin-transition temperature in complexes with tris(pyrazolyl) ligands

By Paulsen, Hauke; Duelund, Lars; Zimmermann, Axel; Averseng, Frederic; Gerdan, Michael; Winkler, Heiner; Toftlund, Hans; Trautwein, Alfred X.
From Monatshefte fuer Chemie (2003), 134(2), 295-306. Language: English, Database: CAPLUS, DOI:10.1007/s00706-002-0522-7

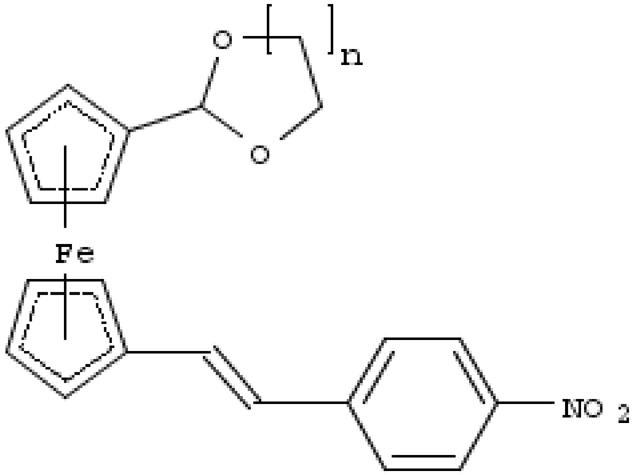
Fe(II) complexes with substituted tris(pyrazolyl) ligands, which exhibit a thermally driven transition from a low-spin state at low temps. to a high-spin state at elevated temps., were studied by Mossbauer spectroscopy and magnetic susceptibility measurements. From the obsd. spectra the molar high-spin fraction and the transition temp. were extd. All substituents, except for Br, lead to a decrease of the transition temp. D. functional calcns. were carried out to compare the exptl. obsd. shifts of the transition temp. with those derived from theory.

~37 Citings

21. A novel and perfectly aligned crystal of a ferrocenyl chromophore displaying high quadratic nonlinear optical bulk efficiency

By Chiffre, Jerome; Averseng, Frederic; Balavoine, Gilbert G. A.; Daran, Jean-Claude; Iftime, Gabriel; Lacroix, Pascal G.; Manoury, Eric; Nakatani, Keitaro
From European Journal of Inorganic Chemistry (2001), (9), 2221-2226. Language: English, Database: CAPLUS, DOI:10.1002/1099-0682(200109)2001:9<2221::AID-EJIC2221>3.0.CO;2-I

The highest nonlinear optical bulk efficiency for a 2-(4-nitrophenyl)ethenylferrocene (140 times that of urea) has been achieved for complex E-I (n = 1) owing to a favorable noncentrosym. packing in which all mols. are perfectly aligned (P1 space group). The crystal structures of I (n = 1, 2) were detd.



I

~28 Citings

22. Enhanced second harmonic generation on passing from a mono- to a dicopper(II) bis(salicylaldiminato) schiff base complex

By Averseng F; Lacroix P G; Malfant I; Perisse N; Lepetit C; Nakatani K
From Inorganic chemistry (2001), 40(15), 3797-804, Language: English, Database: MEDLINE

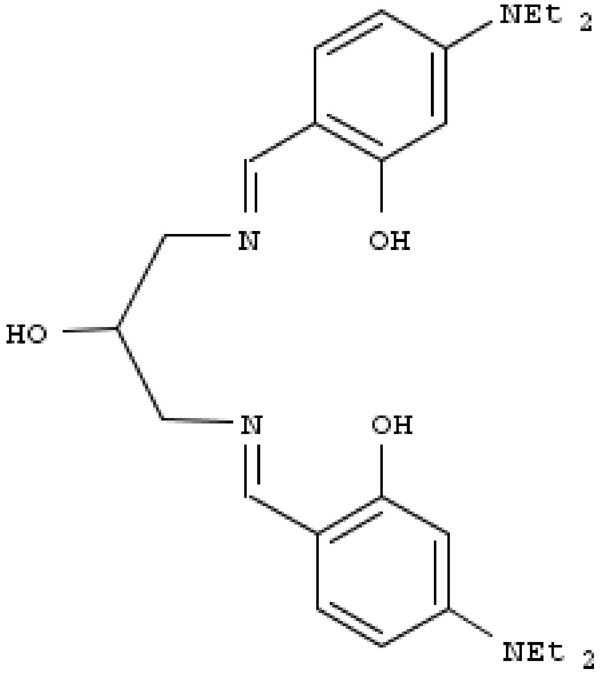
A new ligand (H2LOH) obtained from the Schiff base condensation of 4-(diethylamino)salicylaldehyde with 1,3-diamino-2-propanol is reported, which yields two different copper(II) complexes: CuLOH and Cu2LO(AcO). Crystal data are as follows. CuLOH*EtOH: monoclinic, P2(1)/n, a = 17.810(2) A, b = 8.515(1) A, c = 18.912(2) A, beta = 112.72(1) degrees, Z = 4. Cu2LO(AcO)*1/2H2O: monoclinic, P2(1)/c, a = 21.407(4) A, b = 15.308(2) A, c = 20.156(3) A, beta = 116.83(2) degrees, Z = 4. Cu2LO(AcO)*1/2H2O is antiferromagnetically coupled with J = -207.7 cm(-1) (J being the parameter of the exchange Hamiltonian H = -J S(A).S(B)). CuLOH and Cu2LO(AcO) exhibit good transparencies in the visible frequency range with absorption maxima at 353 and 372 nm, respectively. An enhancement of 83% of the quadratic hyperpolarizability (beta) is observed by the electric field induced second harmonic (EFISH) technique on passing from the mono- to the dinuclear species. Qualitative ZINDO/SCI quantum-chemical predictions give a satisfactory account for this enhancement. The spin dependence of the NLO response of Cu2LO(AcO)*1/2H2O is found to be negligible within the framework of the DFT theory.

~3 Citings

23. Enhanced Second Harmonic Generation on Passing from a Mono- to a Dicopper(II) Bis(salicylaldiminato) Schiff Base Complex

By Averseng, Frederic; Lacroix, Pascal G.; Malfant, Isabelle; Perisse, Nicolas; Lepetit, Christine; Nakatani, Keitaro
From Inorganic Chemistry (2001), 40(15), 3797-3804. Language: English, Database: CAPLUS, DOI:10.1021/ic0013429

A new ligand (H_2LOH, I) obtained from the Schiff base condensation of 4-(diethylamino)salicylaldehyde with 1,3-diamino-2-propanol is reported, which yields two different Cu(II) complexes: CuLOH and $Cu_2LO(AcO)$. Crystal data are as follows: CuLOH·EtOH: monoclinic, space group $P2_1/n$, a 17.810(2), b 8.515(1), c 18.912(2) Å, β 112.72(1)°, Z = 4; $Cu_2LO(AcO)\cdot{}^1/_2H_2O$: monoclinic, space group $P2_1/c$, a 21.407(4), b 15.308(2), c 20.156(3) Å, β 116.83(2)°, Z = 4. $Cu_2LO(AcO)\cdot 1/2\ H_2O$ is antiferromagnetically coupled with $J = -207.7\ cm^{-1}$ (J being the parameter of the exchange Hamiltonian $H = -J\ S_A.S_B$). CuLOH and $Cu_2LO(AcO)$ exhibit good transparencies in the visible frequency range with absorption maxima at 353 and 372 nm, resp. An enhancement of 83% of the quadratic hyperpolarizability (β) is obsd. by the elec. field induced 2nd harmonic (EFISH) technique on passing from the mono- to the dinuclear species. Qual. ZINDO/SCI quantum-chem. predictions give a satisfactory account for this enhancement. The spin dependence of the NLO response of $Cu_2LO(AcO)\cdot{}^1/_2H_2O$ is negligible within the framework of the DFT theory.



I

~42 Citings

24. Synthesis, crystal structure and solid state NLO properties of a new chiral bis(salicylaldiminato)nickel(II) Schiff-base complex in a nearly optimized solid state environment

By Averseng, Frederic; Lacroix, Pascal G.; Malfant, Isabelle; Dahan, Francoise; Nakatani, Keitaro
From Journal of Materials Chemistry (2000), 10(4), 1013-1018. Language: English, Database: CAPLUS, DOI:10.1039/a910244m

A new chiral ligand based on the condensation of 4-diethylaminosalicylaldehyde with (1R,2R)-(+)-1,2-diphenylethylenediamine (H_2L^2) is reported along with its Ni(II) complex. The diamagnetic NiL^2 complex exhibits an efficiency 13 times that of urea in 2nd harmonic generation at 1.9 mm. The structure-property relations are discussed from the crystal structure, in relation with that of a previously reported deriv. which possesses the same mol. NLO response, but very different crystal structure.

~40 Citings

25. Theoretical Investigation of the Effect of a Spin Transition on the Second-Order Molecular Hyperpolarizability of a Bis(salicylaldiminato)FeII Schiff Base Complex

By Averseng, Frederic; Lepetit, Christine; Lacroix, Pascal G.; Tuchagues, Jean Pierre
From Chemistry of Materials (2000), 12(8), 2225-2229. Language: English, Database: CAPLUS, DOI:10.1021/cm001015z

The INDO-based sum-over-states (SOS) perturbation theory and the d. functional theory (DFT) are used to explore the effect of a spin-crossover phenomenon on the quadratic mol. NLO response (β) of an $Fe^{II}L$ complex in which the H_2L ligand is obtained from the Schiff base condensation of 5-nitrosalicylaldehyde with 1,4,7,10-tetraazadecane. The calcns. based on crystal structures recorded at different temps. reveal that the spin transition results in a β increase of about 25% of its initial value. This effect is mainly due to geometry modifications occurring upon spin transition. In addn., a temp. dependence of β is also pointed out for the first time.

~36 Citings

26. Synthesis, Crystal Structure, and Second-Order Nonlinear Optical Properties of a New Bis(salicylaldiminato)nickel(II) Metal Complex

By Averseng, Frederic; Lacroix, Pascal G.; Malfant, Isabelle; Lenoble, Geraldine; Cassoux, Patrick; Nakatani, Keitaro; Maltey-Fanton, Isabelle; Delaire, Jacques A.; Aukauloo, Ally
From Chemistry of Materials (1999), 11(4), 995-1002. Language: English, Database: CAPLUS, DOI:10.1021/CM980650Q

The synthesis, crystal structure, electronic and 2nd-order nonlinear optical (NLO) properties of a new bis(salicylaldiminato)nickel(II) Schiff-base complex are reported. The compd. crystallizes in the space group $P\bar{1}$. The NLO properties were studied by elec. field induced 2nd harmonic (EFISH) and by INDO/SCI-SOS calcn. This compd. obtained by condensation of 4-(diethylamino)salicylaldehyde and 1,2-diamino-4,5-dinitrobenzene in the presence of $NiCl_2$ exhibits the largest 2nd-order NLO response reported for this family of bis(salicylaldiminato)nickel(II) metal complexes, with a $\beta \times \mu$ value of 1530×10^{-48} cm^5 esu^{-1}. A thermal stability up to 300°, indicates potential uses of metal-salen derivs. in poled polymers matrix with high T_g.

~69 Citings