Analysis of "Favorable Growth Element" Based on Rare Earth-aluminum Composite Mechanism of Compound Process

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Abstract. Under the background that failure resulted in by high temperature once only aluminum oxide is used as the gasoline additive. This paper, with the purpose to solve this problem, is to synthesize AcAl oxide for gasoline additive. In order to get the rare-earth-aluminum oxide, first, a complex model of rare earth oxide based on theories about ion coordination is established. Then, by the complex model, the type of "compound growth unit" when rare earth elements join the hydrothermal conditions and the inclination that "diversification" might probably happen are deduced. Depending on the results got by complex model, this paper introduces the type of compound and its existence conditions of "Compound growth unit" owned by stable rare-earth-aluminum oxide. By adjusting the compositions of modifier, compound materials of rare earth-aluminum oxide used for gasoline additive is made. By XRD test, aperture test, adsorption test and desorption test, the theoretical deduction is proved to be right. From the experiment, it is concluded that: a dense environment is the pre-condition to form rare-earth-aluminum polymer, which is also an essential condition for the polymer to update to a favorable growth unit and produce mesoporous rare-earth-aluminum oxide with high activity.
Keywords: Gasoline additive; Rare-earth-aluminum complex model; Compound growth unit; Favorable growth unit.

1. Introduction

Normally, if automobile exhaust needs to be treated in an efficient way, it is mandatory to have a high-efficient catalyst and a carrier which is able to covert hazardous gas into harmless substances. Nanometer $A1_2O_3$ is able to oxidize CO and deoxidize nitrogen oxide because there are many dangling bonds the adsorption is quite good. Therefore, the automobile exhaust can be converted into harmless gas ---CO_2 and nitrogen. For rare earth elements, they can enhance the activity of gasoline and lower the ignition point, which can prevent the unsaturated carbon nitride compound resulted in by that the gasoline is not fully burned. According to relevant references [1]-[4]: for rare earth compound, its nanometer powder has an extraordinary performance in oxidation- reduction. Once rare earth compound is used, the contamination made by CO and NOX existed in automobile exhaust can be cleared out. The updated nanometer catalyst will play an active role in catalyzing the gasoline, which requires no exhaust purification because CO and NOX will not be produced when the gasoline is burning.

This paper is to discuss the establishment of complex model for gasoline additive rare-earth-aluminum and the model of compound growth unit. By synthesis, an element able to absorb

rare earth, whose carrier is aluminum oxide is formed. Then a new compound material -- rare-earth-aluminum oxide aperture is obtained, which can be used as a new gasoline additive. By such a new material, a "microreactor" concentrated on nanometer material will be generated, where the gasoline burning will be catalyzed and PM2.5 in the exhaust will be reduced.

2. Experiment Conditions

Experiment materials: main materials used by this experiment include Rare earth, sodium aluminate, sodium hydroxide, hydrochloric acid and absolute ethyl alcohol, which are all produced by Beijing Yili Fine Chemicals Co., Ltd. These materials are analytically pure. This experiment also uses some auxiliary additives like lauryl sodium sulfate, SDBS (sodium dodecyl benzene sulfonate) and hexadecyl methyl ammonium bromide.

3. Establishment of Rare Earth Aluminum Compound Composite Molecular Model and Growth Unit Motion Prediction

3.1. Rare-earth-aluminum Structure

Ce has a unique 4f electronic structure, cerium oxide has a face-centered cubic structure (cubic system). for the face-centered cubic structure, it is not arranged densely. In this way, oxygen vacancy will be resulted in. For its point group, Fm3m point group existed. From the view of thermodynamics, its (111) side is the most stable. For the unit cell CeO_2, Ce^{4+} is arranged in the way of face-centered cubic structure, O^{2-} occupies all the tetrahedrons, each single Ce^{4+} is surrounded by 8 O^{2-} while each single O^{2-} have a coordination with 4 Ce^{4+}. Refer to Fig. 1:

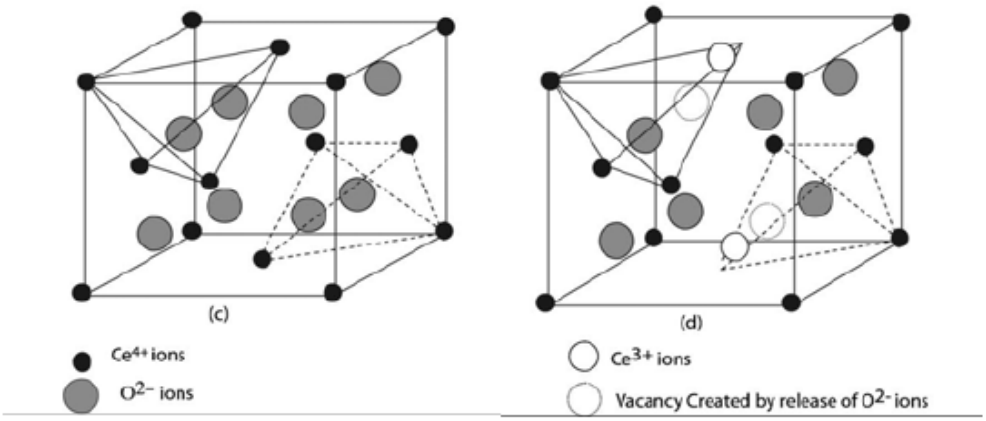


Figure 1. CeO_2 Structure

After a high temperature (T>950 ℃) reduction, cerium oxide will become CeO_{2-x} oxide ($0<x<0.5$) which has oxygen vacancy and non-stoichiometric ratio. If at a low temperature (T<450 ℃), CeO_2 might become a series of compounds with different compositions. Although a certain quantity of oxygen is lost by crystal lattice, which makes large amounts of oxygen vacancy formed, CeO_2-x can still tightly hold its fluorite-like crystal structure. For such a metastable oxide, once it is exposed at a place easy to have oxidation, it will be changed into CeO_2 easily. Therefore, we can say that CeO_2 has an excellent ability in storing and releasing oxygen, as well as the ability to have redox reaction. If so, the quantity of oxygen atom existed in the crystal structure will change, making the ability to store and release oxygen available.

Being as a catalyst, aluminum oxide are easy to changed into α-Al_2O_3 when the temperature is as high as 1000~1600℃. It is known that α-Al_2O_3 is the variant whose structure is the most dense and whose activity is the lowest. Its structure is quite stable. The struct is shown in Fig. 2:

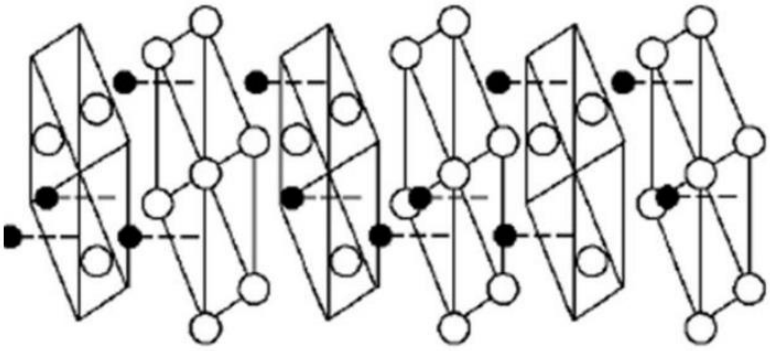


Figure 2. α-Al_2O_3 Structure

For an ideal Rare earth aluminum compound catalyst, it shall be a compound oxide whose carrier shall be aluminum oxide and which will have a sequential aperture structure after adsorbing Rare earth. Ce^{4+} will be adsorbed on the surface of aluminum oxide. By rare earth element, a transfer between ion 3^+ and ion 4^+ can be obtained. In this way, a strong ability in getting and losing electron will be formed, as well as the ability of redox reaction.

3.2. Establish Rare earth-aluminum "Composite Molecular Model"

γ—AlOOH belongs to orthorhombic system, The crystal structure is arranged (010), with a shape of storey. Refer to Fig.3 for the structure:

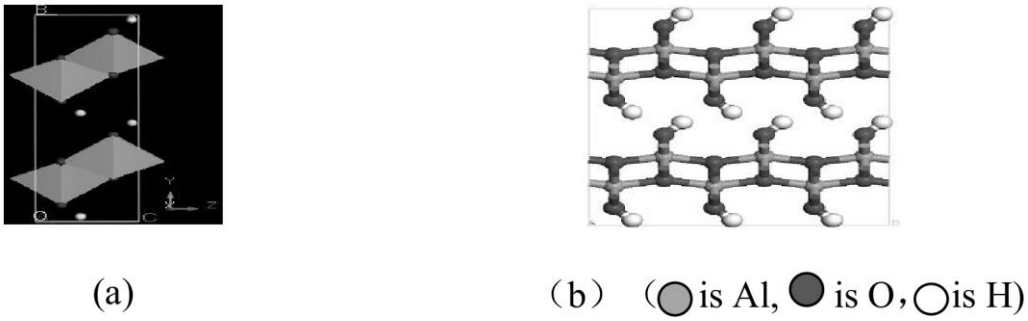


Figure 3. γ—AlOOH Crystal Structure and Arrangement of Internal Atoms

Based on the coordination principle of anion of metal cation, the hydrolysis structure and "isomorphous replacement" of the metal cations, here below is the Rare earth aluminum complex model. Refer to Fig.4 for the Composite molecular model.

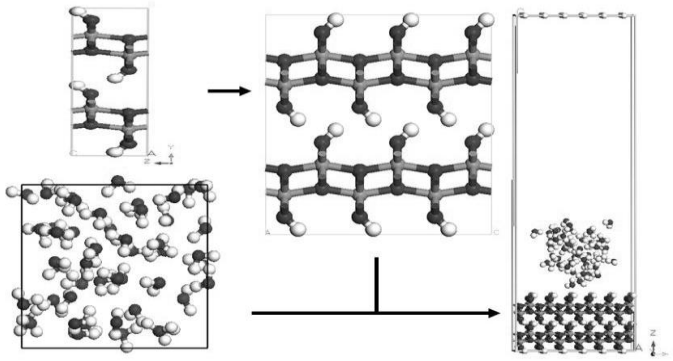
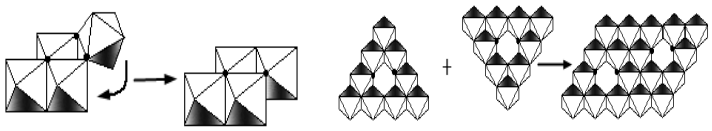


Figure 4. Rare earth aluminum Composite molecular model (is Al, is O, is element H is rare earth element)

3.3. Motion Analysis for Rare earth - aluminum "Compound Growth Unit"

According to our experience [5]-[8], it is able to deduce the "compound growth unit" and "favorable growth unit" where rare earth elements join the hydrothermal conditions. The growth unit might be in the form of "diversification" -- different kinds of "aggregation" are co-existed. Rare earth element or ion can have a bridging reaction with [Al(OH)3(OH2)3]0 (a kind of unimer stably existed in the solution), with dimer produced, including [Ce Al2(OH)9(OH2)3]0, [La Al2(OH)9(OH2)2]0 and [YbAl2(OH)9(OH2)]0. Then bridging with [Al(OH)3(OH2)3]0 (neutral unimer), "trimer" will be formed, which will update as "favorable growth unit".

In the dilute solution, "trimer" will not be existed as a "favorable growth unit". however, in strong solution, the neutral trimer can bridge with [Al(OH)3(OH2)3]0 (neutral unimer), with " tetramer" formed. Then, the tetramer will update to "favorable growth unit". Refer to Fig. 5:



(a) Trimer (b) Polymer

Figure 5. Motion of Rare earth aluminum Compound Growth Unit

In the experiment, surface modifiers can be added, whose content of different compositions shall be well controlled in order to have a strong environment which is consistent with the requirements of rare-earth-aluminum "compound favorable growth unit". In this way, it will be beneficial for rare-earth-aluminum "favorable growth unit".

4. Analysis on Rest Result

Refer to Fig. 6 for SEM and adsorption result.

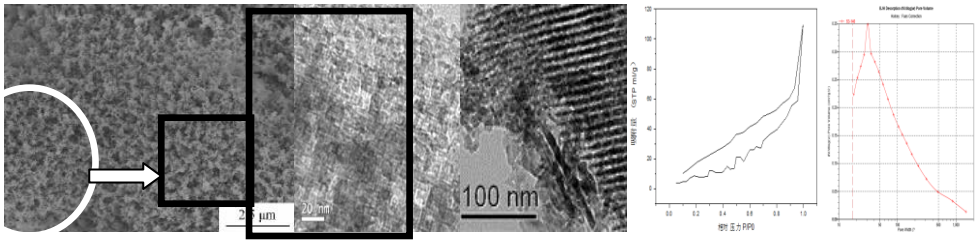
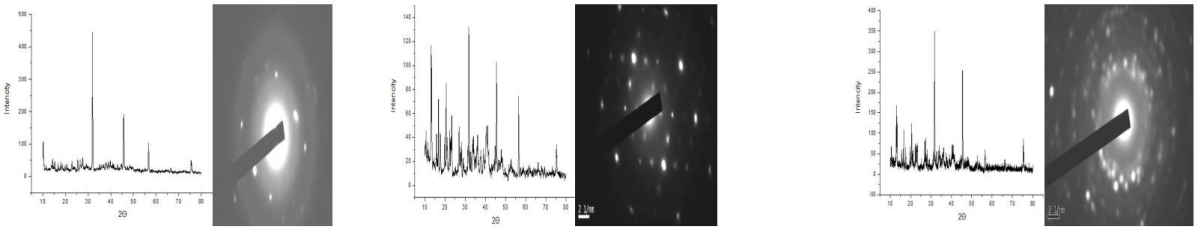


Figure 6. Motion Model of Rare earth aluminum Compound Growth Unit

From the figure, we can see that the synthesized rare-earth-aluminum compound have 20-30 aperture structure. After the adsorption and desorption, it has a good chemical activity.

Fig.7 is the XRD analysis for the experimental sample and its lattice structure. (a), (b) and (c) are the samples with yttrium, lanthanum and cerium added.



(a) yttrium-aluminum compound oxide (b) Lanthanum-aluminum compound oxide (c) cerium-aluminum compound oxide

Figure 7. EDS of Experimental Samples

We can see peak with characters of aluminum oxide and rare-earth oxide and peak with the varied rare-earth oxide are existed. Because the atom radius of rare earth element is 173.5pm~187.9pm, ion radius is 85pm~106pm. That is the radius of atom and ion are much more than the commonly-seen metal atoms and ions, so when rare earth is being modified, isomorphous replacement will happen, as well as vacancy doping. This is proved by lattice structure.

5. Conclusion

Based on the anion coordination theory, Rare earth aluminum Composite molecular model is established, by which the type of "compound growth unit" when rare earth elements join the hydrothermal conditions and the inclination that "diversificatio n" might probably happen are deduced. According to the deduction, it is concluded that strong environment is an essential condition for rare-earth-aluminum "compound growth unit" poly mer. Once polymer is obtained, polar ion shall be added can favorable growth unit be generated. By adding modifier and adjusting the compositions, it is proved that the theoretical deduction is correct. Here below are the final conclusions:

(1) Rare-earth-aluminum compound oxide, when being compounded, trimer growth unit is formed via isomorphous replacement; meanwhile, complex polymer will be also formed via vacancy doping. The growth unit and complex polymer will be updated once there is a strong environment, with "favorable growth unit" generated.

(2) Rare-earth-aluminum compound oxide has aperture structure, which is proved to have a good catalyst activity by aperture test, adsorption test and desorption test.

6. Acknowledgement

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7. References

[1] Shi Erwei etc. Hydrothermal Crystallography [M]. Beijing Sciences Press, 2004.In Chinese.
[2] Yang Jing. Purification of Automobile Exhaust [J]. Environmental Science, 2014, 43(8): 24-26.In Chinese.
[3] Lin Huibin, Cai Ruibin and Liang Jingming. Study on Impact on Automobile Exhaust Purification and Energy-saving by Gasoline Additive [J]. Lubrication Engineering, 2004(1): 38—40.In Chinese.
[4] Yi Shi and Liu Rongli. Research and Application of Rare Earth Catalyst in Environmental Protection [J]. Technical and Engineering Application, 2014, 30-33. In Chinese.
[5] Hao Baohong and Fang Keming. Analysis on Nanometer AlOOH "Favorable Growth Unit" under Compound Additive [J]. Contemporary Chemical Industry, 2011, 40(3): 307-310.In Chinese.
[6] Hao Baohong, Duan Qiutong and He Qi etc. R&D of "Rare-earth-aluminum" Nanometer Catalyst and its Application in Purifying Automobile Exhaust [J]. Contemporary Chemical Industry, 2013, 42 (6): 810-812.In Chinese.

[7] Hao Baohong, He Qi,Zeng Qihui and Yang Qianqian. Micro-crystal structure analysis about precursor AlOOH of nano-alumina [J]. Integrated Ferroectrics.167 (01):220-226.In Chinese.
[8] Hao Baohong, Zhu Ling, Deng Quanyong,Yang Xuguang, Cheng Hanzhang .The Two Types of “Coalescence Growth” of Nano-AlOOH under Hydrothermal Conditions [J]. Integrated Ferroectrics.167 (01): 227-235. In Chinese.