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Spectroscophical Study on Activated Mn(Ⅱ) Oxide Added La_2O_3 for Trace Oxygen Removal

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Abstract We have spectroscophically considered the reason which deoxidation volume has been improved as La_2O_3 was added in Mn(Ⅱ) oxide to remove the trace oxygen in various kinds of gases such as hydrogen, nitrogen and argon. La_2O_3 makes dispersion of Mn(Ⅱ) oxide good as it makes activated composition crystalline particle small and keeps dispersion of activated composition quiet as Mn-O-La type bond is formed in its surface.

Key words manganese oxides, deoxidation, Perovskite type oxide

Introduction

The great leader Comrade **Kim Jong Il** said as follows.

"**Scientists and technicians should work to overcome by their own efforts the problems which require an urgent solution for the development of the national economy of our country, and to introduce the scientific and technical successes of developed countries in accordance with its specific reality.**"("**KIM JONG IL** SELECTED WORKS" Vol. 10 P. 195～196)

To remove completely the microimpurities oxygen in the material gases such as hydrogen, nitrogen and argon is very important in the high purity material industry and advanced technology research works.

The methods for deoxidation in gases are generally two methods, that is, one is removal with water by hydrogenation of oxygen over various precious metal catalysts and the other is method using the oxidation of metal or metal oxides [1, 9, 10, 12].

In the first method, in case of all gases except hydrogen, hydrogen more than oxygen stoichiometrically corresponding to trace oxygen in it must be added and water got by hydrogenation of oxygen and excessive hydrogen put for deoxidation must be removed in the purification of gases unneeded hydrogen as well as oxygen.

Second method, that is, deoxidation method using oxidation of metal or metal oxides has been using because of relatively sampling and convenience.

The research paper which Mn(Ⅱ) oxide plated in various kinds of carriers can remove the oxygen under for less than 10^{-9}% has been already found [3], but it has been used in the only experimental scope because its deoxidation volume is very small. Specially, deoxidation method using Mn(Ⅱ) oxides has been giving attention because of almost completely deoxidation in the material gases.

When La_2O_3 is added with 6% in pure Mn(Ⅱ) oxide, it not only deoxidation volume gets increased but recycling propertity gets better [1].

Also when La is added, the oxides of Mn or Cu are dispersed better on the alumina surface, get well reducibility by hydrogen[8] and La_2O_3 is dispersed easily and diffraction peaks of crystal form do not appear although content of it is 20% [11].

However, they have not explained the reason getting better dispersity when La_2O_3 is added.

We have studied the reason the deoxidation volume gets increased and recycling propertity gets better by adding La_2O_3 with 6% in the Mn(Ⅱ) oxide in the viewpoint of spectroscopy.

Experiment

Absorbents preparation **A**ll absorbents were prepared with the wet mixed way using $MnCO_3$(99.8%), La_2O_3(99.9%), clay and $Mn(NO_3)_2$ solution (40%) and then dried and calcined at 200℃ for 1.5h in the air and reduced with hydrogen at 450℃ for 2h.

Absorbents characterization Infrared absorption spectrum analysis carried out using infrared spectroscopy(“FTIR-8101”) and X-ray diffraction(XRD) spectra were obtained using X-ray diffraction analysis(“MINIFLEX”, CuK_α λ=0.154 2nm).

Results and Discussion

To study the reason increased the deoxidation volume when La_2O_3 is added, XRD patterns of deoxidation and FT-IR spectrums of several samples have taken place.

XRD patterns of several samples are as Fig. 1.

As shown in Fig. 1, in case of sample (4) added clay and La_2O_3 in the Mn oxide, diffraction peaks of MnO and Mn_3O_4 appear most dull. This means that activated component MnO crystal particle gets small because of adding of La_2O_3.

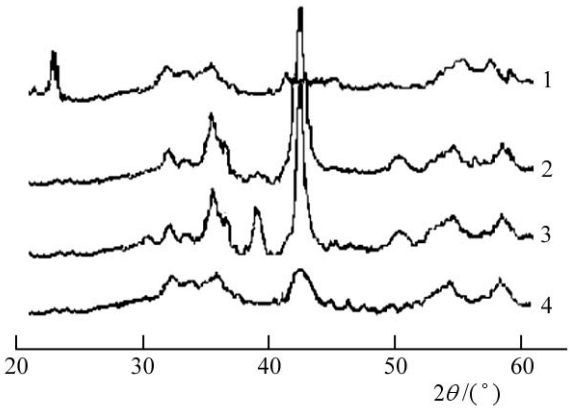

Fig. 1. XRD patterns of several samples
1－clay, 2－Mn_XO_Y, 3－Mn_XO_Y-clay,
4－Mn_XO_Y-La_2O_3-clay

To consider what happening the phenomenon in the surface of adsorbent in case of adding La_2O_3 FT-IR spectrums of samples dried and calcined in the air at 200 ℃ for 1.5h are as Fig. 2.

As shown in Fig. 2, absorption bands at 1 087, 868, 726cm^{-1} correspond to manganese carbonate [6], absorption bands at 1 100, 1 000～1 050cm^{-1} in clay or sample added clay

correspond to valence vibration of Si-O in clay, absorption band at 920cm^{-1} correspond to Al-O-H in clay and absorption band at 550 cm^{-1} correspond to Si-O-Al [2, 5, 7].

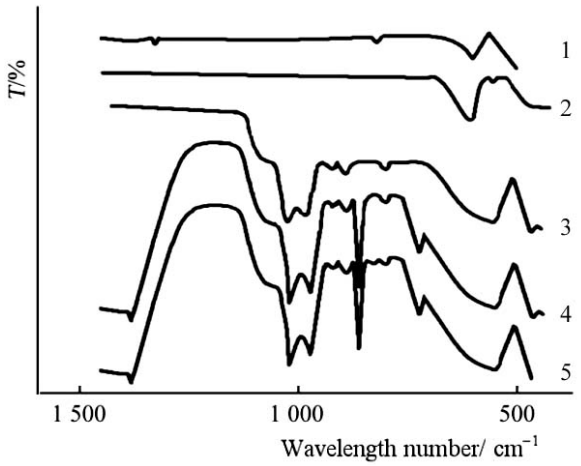

Fig. 2. FT-IR spectrums of several samples
1－MnO_2, 2－La_2O_3, 3－clay, 4－Mn_XO_Y-clay,
5－Mn_XO_Y-La_2O_3-clay

Here what catches the eye is the absorption bands at 820cm^{-1}.

According to the precedent literature [11], absorption band by skeletal vibration corresponding to M_1-O-M_2 type bond (where M_1, M_2 are different metals) appears at 800 ～900cm^{-1}.

Considering our experimental tests in the light of this precedent research paper, we can find that a weak peak at near by 820cm^{-1} correspond to Mn-O-La bond in case of absorbent added La_2O_3.

Changing the content of La_2O_3 to confirm this fact, FT-IR spectrums considering the change of absorption band at 820cm^{-1} are as Fig. 3.

As shown in Fig. 3, as content of La_2O_3 is increased differences don't appear in another absorption peaks, absorption band but at 820cm^{-1} gets strengthened.

This fact means that the bond across oxygen between activated component Mn and promoter La in the case of adding La_2O_3 is completely formed in the drying and calcinating course at 200℃ in the air.

Fig. 4 shows XRD patterns of absorbents manufactured by mixing with $MnCO_3$: La_2O_3 : clay＝4 : 3 : 3 and impregnating several times with $Mn(NO_3)_2$ solution 20% of whole weight, dried and calcined at 200℃ in the air.

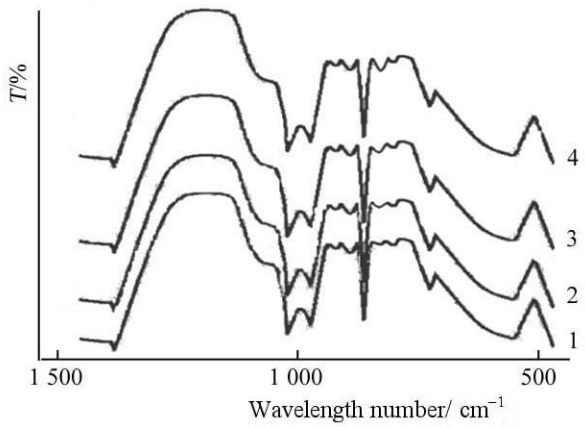

Fig. 3. FTIR spectrums strength change at 820cm^{-1} according to La_2O_3 content.
1－4 are 6, 10, 20 and 30% respectively

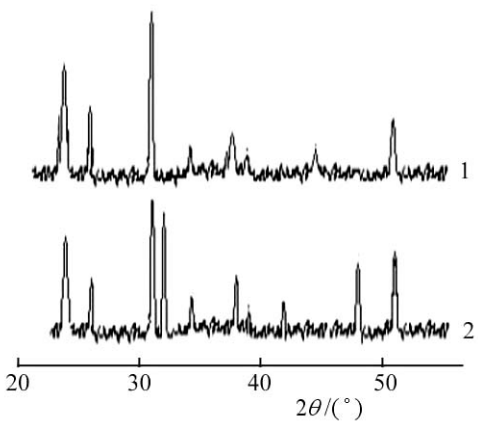

Fig. 4. XRD patterns to check the formation of La-O-Mn bond compound
1－Mn_XO_Y-clay, 2－Mn_XO_Y-La_2O_3-clay

According to XRD manual datas and precedent literatures[4], XRD peaks of $LaMnO_3$ compound of Perovskite type appear at 2θ 32.5, 47.5, 42° and as shown in Fig. 4 peaks of $LaMnO_3$ obviously observed at 32.5, 47.5, 42° .

This means that in the dring and calcining course of absorbents preparation stage at 200℃ in the air manganese oxides and La_2O_3 interact to form Perovskite type complex oxide and formed complex oxide is equally dispersed on the absorbent surface deoxidation capacity gets high.

Conclusion

When La_2O_3 is added, in the 200℃, air in the drying and calcining course of absorbents preparation Perovskitetype complex oxide having Mn-O-La bond is formed to get fine and in the surface of activated composition particle Mn-O-La bond is formed and as it keeps dispersion of activated composition quiet deoxidation capacity gets high and recycling property gets better.

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