Experimental and Theoretical Studies on the Influence of Carrier Gas for COS Catalytic Hydrolysis over MgAlCe Composite Oxides

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ABSTRACT: Catalytic hydrolysis of carbonyl sulfide (COS) over metal frameworks derived MgAlCe composite oxides catalyst is investigated under N2 and CO atmosphere. A combination of experimental and theoretical methods, including in situ IR, X-ray photoelectron spectroscopy, and density functional theory calculations, is used to explain the difference of catalytic activity. Research results indicate that M−OH groups play the most important role in COS hydrolysis, but the distribution of the M−OH groups is affected by CO. There is no competitive adsorption effect between N2 and COS on the surface of catalyst but CO and COS. Meanwhile, the hydrolysis reaction of COS is an instantaneous reaction and a noninstantaneous reaction under N2 and CO atmosphere, respectively. In general, under N2 atmosphere, COS is directly adsorbed on the surface of the catalyst and most of the −OH groups are adsorbed as M−OH formation. Under CO atmosphere, most of the active sites occur as CO due to the competitive adsorption effect.

1. INTRODUCTION

Carbonyl sulfide (COS) is one of the main organic sulfur compounds in industrial tail gases, such as closed carbide furnace tail gas, coke oven gas, and yellow phosphorus tail gas.1−3 In these industrial tail gases, CO (>75%) is an important resource for C1 chemical industry. However, the existence of COS is not conducive to the purification of CO, which leads to environmental pollution and equipment corrosion.4−6 Therefore, it is important to remove COS from these industrial tail gases. So far, catalytic hydrolysis method is regarded as the suitable way for the removal of COS because of high removal efficiency, low operation cost, and mild reaction condition.7−11 The hydrolysis products of COS are CO2 and H2S.12−16 H2S can be removed more easily than COS. In our previous study, hydrotalcite-like compounds-derived MgAlCe composite oxides (MgAlCeOx) show 100% COS removal efficiency under N2 atmosphere condition.17 However, the main component in industrial gas is CO. The carrier gas condition can change the removal efficiency and process. Therefore, it is necessary to investigate the effect of carrier gas for COS removal process.

In this work, MgAlCeOx is prepared for catalytic hydrolysis of COS. The influence of carrier gases (CO and N2) is investigated by experiment and density functional theory (DFT) calculation. In situ IR and X-ray photoelectron spectroscopy (XPS) analyses are used to further explain and carry out the removal process of COS over MgAlCeOx under different carrier gas conditions.

2. RESULTS AND DISCUSSION

2.1. Effect of N2 and CO Atmosphere on Catalytic Activity. The catalytic activity of MgAlCeO3 under CO and N2 is shown in Figure 1. H2S can be detected at the outlet of
the reactor, which indicates that the removal of COS is a catalytic hydrolysis process. As seen in Figure 1, COS conversion rate keeps 100% for 60 min and then decreased over time under N2 atmosphere. However, COS conversion rate first increases from 83 to 88% (at 40 min) and then decreases over time under CO atmosphere. It indicates that carrier gas affects the removal process of COS. The difference is attributed to the interaction of the catalyst and COS/N2/CO, and the competitive adsorption among COS/N2/CO. Furthermore, COS conversion rate under N2 atmosphere is still higher than that under CO atmosphere. It shows that MgAlCeOx has lower catalytic activity in the industrial gas than that in the N2 atmosphere. To find out the detailed effect of carrier gas, in situ IR, XPS analyses, and DFT calculation are carried out.

2.2. In Situ IR Analysis. To investigate the change of surface functional groups on the catalysts under CO and N2, in situ IR is carried out and is shown in Figure 2. From Figure 2, these peaks located at 3600−3700 cm−1 are attributed to the vibration of −OH groups, including linear −OH groups M−OH (at 3697 cm−1), bridged bonded −OH groups M−(OH)−M (at 3664 cm−1), and triply bonded −OH groups M−(M−OH)−M (at 3631 cm−1). The peak located at 1726 cm−1 is attributed to the vibration of the ==C==O groups.

From Figure 2a, linear −OH groups M−OH are the main −OH groups under N2 atmosphere. From Figure 2b, bridged bonded −OH groups M−(OH)−M and triply bonded −OH groups M−(M−OH)−M are the main −OH groups under CO atmosphere. It indicates that the species of −OH groups is affected by N2 and CO, which might be attributed to the competitive adsorption effect between −OH groups and N2/CO. Under N2 atmosphere (in Figure 2a), the peak intensity of the M−OH and ==C==O groups decreases over time, indicating that the M−OH and ==C==O groups participate in the hydrolysis reaction. Under CO atmosphere (in Figure 2b), the peak of M−OH is weakened over time, but there is no obvious change for M−(OH)−M, M−(M−OH)−M, and ==C==O groups. It indicates that M−(OH)−M and M−(M−OH)−M groups have less promotional effect on COS hydrolysis. Coupled with the catalytic activity results shown in Figure 1, M−OH groups play the most important role in COS hydrolysis.

CO is a polar molecule, and it might be adsorbed on the surface of the catalyst. Under CO atmosphere, the amount of M−(OH)−M and M−(M−OH)−M groups are higher than that of M−OH groups, which indicates that CO has a competitive adsorption effect on −OH groups. It leads to the fact that most −OH groups appear on the surface of the catalyst in the formation of M−(OH)−M and M−(M−OH)−M. As a result, less M−OH groups provide less catalytic activity. Furthermore, the amount of CO is higher than COS, which leads to a competitive adsorption effect between COS and CO. Because the dipole moment value of COS is bigger than CO, COS would adsorb on the surface of the catalyst after CO. Therefore, COS removal rate is lower under the industrial atmosphere (CO) than under N2 atmosphere. The in situ IR results are in agreement with the experimental results. According to the above in situ IR results and the

Figure 2. In situ IR experiments of COS removal over MgAlCeOx under (a) N2 and (b) CO atmosphere (reaction condition: 470 ppm COS, 2.67% RH, 5000 h−1 GHSV, reaction temperature = 50 °C).
experimental results, the distribution of different −OH groups on the surface of catalyst is shown in Figure 3.

**2.3. XPS Analysis.** To further investigate the difference of catalytic activity under CO and N\textsubscript{2} atmosphere, XPS characterization is carried out and used to examine the composition of different metals on the surface of catalyst.\textsuperscript{18} It provides a basis for constructing a computational model. As shown in Figure 4, Mg−O (49.6 eV), Al−O (74.3 eV), and Ce−O (882.1 eV) are the principal formations for Mg 2p, Al 2p, and Ce 3d, respectively. Based on the C content, the relative contents of Mg, Al, and Ce are calculated, and the relative proportions of Mg, Al, and Ce are shown in Table 1.

From Table 1, Al content is highest and Ce content is lowest. However, in the preparation of catalyst, Mg content is higher than the Al content. It is attributed to that part Mg adsorbs on the inner surface of crystal. According to above XPS results, the structure of MgAlCeO\textsubscript{x} crystalline is built and shown in Figure 5a. Meanwhile, MgAlCeO\textsubscript{x} (110) surface (in Figure 5b) is used in the following calculation study.

**2.4. Competitive Adsorption of CO and COS on the Surface of Catalyst.** According to the in situ IR results in Figure 2, CO has a competitive adsorption effect with −OH groups and COS. To further investigate the competitive adsorption effect between CO and COS, the adsorption energy is calculated and adsorptive site is investigated. From Table 2, the adsorption energy for CO, N\textsubscript{2}, and COS on the surface of MgAlCeO\textsubscript{x} (110) is shown.

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**Table 1. Relative Proportion of Surface Metal Atoms**

| element | Mg | Al | Ce |
|---------|----|----|----|
| proportion (%) | 20 | 77 | 3  |

**Table 2. Adsorption Energy of CO, N\textsubscript{2}, and COS on the Surface of MgAlCeO\textsubscript{x} (110)**

| gas   | COS | CO | N\textsubscript{2} |
|-------|-----|----|------------------|
| adsorption energy (kJ/mol) | −18.27 | −34.39 | >0            |

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Figure 3. Distribution of −OH groups on the surface of catalyst.

Figure 4. XPS characterization results of MgAlCeO\textsubscript{x} (Mg 2p, Al 2p, and Ce 3d).

Figure 5. Crystalline structure of (a) MgAlCeO\textsubscript{x} crystal and (b) MgAlCeO\textsubscript{x} (110) surface.
there is no competitive adsorption effect between N\textsubscript{2} and COS because the adsorption energy between N\textsubscript{2} and catalyst is positive. Furthermore, the adsorption energy (absolute value) between CO and catalyst (34.39 kJ/mol) is higher than that between COS and catalyst (18.27 kJ/mol). It indicates that CO is more easily adsorbed on the surface of catalyst than COS. The adsorption site of CO and COS on the surface of MgAlCeO\textsubscript{x}(110) is shown in Figure 6. As shown in Figure 6a, the adsorption site of CO on the surface of catalyst is C···O (C from CO and O from MgAlCeO\textsubscript{x}(110)), and the bond length value of C···O is 1.412 Å. From Figure 6b, the adsorption site of COS on the surface of catalyst is C···O (C from COS and O from MgAlCeO\textsubscript{x}(110)), and the bond length value of C···O is 1.607 Å. It indicates that CO is more stable than COS when they are adsorbed on the surface of catalyst. Therefore, the hydrolysis reaction of COS is an instantaneous reaction under N\textsubscript{2} atmosphere, and it is a noninstantaneous reaction under CO atmosphere.

Depending upon the above in situ IR and calculation results, the difference of catalytic activity under CO and N\textsubscript{2} atmosphere is shown in Figure 7. As shown in Figure 7, under N\textsubscript{2} atmosphere, COS is directly adsorbed on the surface of the catalyst. Meanwhile, most of the −OH groups are adsorbed as M−OH formation, which could directly react with COS. Under CO atmosphere, most of the active sites occurred as CO, and few COS molecules are adsorbed on the surface of the catalyst. It is attributed to the competitive adsorption effect by COS and CO. Therefore, the noninstantaneous reaction is generated in CO atmosphere. Quantum chemistry calculations corroborate the in situ IR results and provide complementary information concerning the hydrolysis mechanism.

3. CONCLUSIONS

This work systematically investigates the influence of different carrier gases on COS catalytic hydrolysis over MgAlCeO\textsubscript{x}, including N\textsubscript{2} and CO atmosphere. Experimental results indicate that MgAlCeO\textsubscript{x} has lower catalytic activity in the industrial gas than that in the N\textsubscript{2} atmosphere. In situ IR results indicate that linear −OH groups M−OH are the principal −OH groups under N\textsubscript{2} atmosphere. Bridged bonded −OH groups M−(OH)−M and triply bonded −OH groups M−(M−OH)−M are the main −OH groups under CO atmosphere. The M−OH groups play the most important role in COS hydrolysis. CO affects the distribution of different −OH groups on the surface of the catalyst due to the competitive adsorption effect between CO and M−OH. The XPS results show that Mg−O, Al−O, and Ce−O are the main formations for Mg 2p, Al 2p, and Ce 3d, respectively, which provides the surface element proportion for building the crystal structure. The calculation results indicate that CO is more easily and stably adsorbed on the surface of catalyst than COS. Meanwhile, the hydrolysis reaction of COS is an instantaneous reaction under N\textsubscript{2} atmosphere, and it is a noninstantaneous reaction under CO atmosphere. In general, under N\textsubscript{2} atmosphere, COS is directly adsorbed on the surface of the catalyst and most of the −OH groups are adsorbed as M−OH formation. Under CO atmosphere, most of the active sites occurred as CO due to the competitive adsorption effect.

4. EXPERIMENTAL AND THEORETICAL METHODS

4.1. Catalyst Preparation. MgAlCeO\textsubscript{x} is synthesized through our previous method.\textsuperscript{17} The preparation conditions are reproduced below. The atomic ratio of Mg/Al/Ce is 34:16:1, and the mole ratio of NaOH/Na\textsubscript{2}CO\textsubscript{3} is 1:1. The pH
of the mixed metal salt solution is adjusted by adding mixed alkaline solution until pH = 8. The hydrothermal temperature is 140 °C. The calcination temperature is 600 °C and calcination time is 3 h.

4.2. Characterization. XPS (ESCALAB 250) analysis is performed at a base pressure in the analysis chamber of 5 × 10⁻¹⁰ mbar using Al Kα X-ray source with excitation energies of 1486.6 eV. With the total instrumental resolution of 1.18 eV for Al Kα excitation sources spectra is recorded. The energy scale is calibrated by normalizing the C 1s line of adsorbed adventitious hydrocarbons to 285.0 eV. In situ IR spectroscopy is collected using a Nicolet iS50 FTIR spectrometer equipped with a smart collector. The IR spectra are recorded by operating at accumulating 100 scans at a resolution of 4 cm⁻¹.

4.3. Catalytic Activity Measurements. Desulfurization tests are performed in a fixed-bed quartz reactor under atmospheric pressure. The catalytic activity test system is same as our previous system.37 In this study, the reaction conditions are as follows: 470 ppm COS; 2.67% relative humidity (RH); 5000 h⁻¹ gas hourly space velocity (GHSV); and 50 °C reaction temperature. COS and H₂S concentrations of the gas feed and effluent from the reactor are analyzed using a FULI 9790II gas chromatography. COS removal rate is obtained by calculating the inlet and the outlet COS concentrations

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\text{COS conversion(%) = } \frac{\text{COS}_{\text{in}} - \text{COS}_{\text{out}}}{\text{COS}_{\text{in}}} \times 100
\]

4.4. Computational Methods. All calculations in this work are performed using Dmol³ program in the Material Studio 2017 software package.19,20 The molecular geometry (MgAlCeO₆(110), COS, N₂, and CO) and the adsorption energy of COS/CO/N₂ on MgAlCeO₆(110) surface are calculated and optimized using the GGA/PBE method with DNP basis.31 The cell structure of MgAlCeO₆ is set based on MgAlO₃. The tolerance of the SCF, energy, gradient, and displacement convergence are 1.0 × 10⁻⁶ hartree (Ha), 1.0 × 10⁻⁵ Ha, 2.0 × 10⁻⁴ Ha/Å, and 5.0 × 10⁻⁴ Å, respectively. K value is 3 × 2 × 1. The calculations are set to spin unrestricted. Ramirez-Dámaso et al. found that the (110) surface is more reactive than other surface.22 Therefore, the (110) surface is considered in this work. After cleaving the surface, the three-dimensional structure is built with a vacuum slab of 150 nm.

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Notes
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