

Alkaline earth metal oxides on γ -Al₂O₃ supported Co catalyst and their application to mercaptan oxidation

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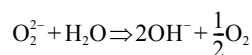
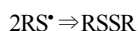
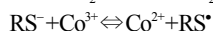
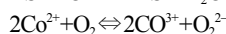
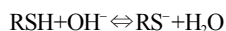
Abstract— γ -Al₂O₃-supported alkaline earth metal oxide samples with different MgO, CaO, SrO and BaO loadings have been prepared by impregnating γ -Al₂O₃ with alkaline earth metal nitrate solutions and then calcining at 773 K and 1,023 K. The resultant samples have been characterized by XRD, EDS coupled with SEM, CO₂-TPD and BET. After preparation of the γ -Al₂O₃-supported alkaline earth metal oxide samples and impregnation with the liquid catalyst LCPs30, supplied by Axens, the catalytic performance of these catalysts was evaluated in the mercaptan oxidation reaction. Results showed that magnesium base oxide is formed at 773 K and base oxides of calcium, barium and strontium are formed at 1,023 K. Catalysts with higher mole ratios have higher conversions and the basicity increases with increasing base oxide loading in the samples. Furthermore, the conversion of mercaptans increases with increasing atomic number of the alkaline earth metal, excluding MgO, which has the highest conversion compared to the other base oxides.

Key words: Mercaptan, Oxidation, Basic Catalyst, LCPs30

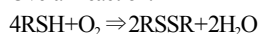
INTRODUCTION

In recent years, due to population growth in industrial areas and environmental problems, the refining industry has been under immense pressure to produce cleaner fuels. Most light oil fractions contain mercaptans, which must be reduced to international standard levels using appropriate methods. Mercaptans, a kind of organic sulfide widely present in petroleum products, often cause foul odors, deteriorate the final petroleum products, and corrode metals due to their acidity. Several processes are used for the removal of mercaptans from petroleum products. The most common practice is to oxidize the mercaptans present to less deleterious disulfides with air in the presence of a catalyst [1,2].

The Merox process for mercaptan oxidation is one of the families of Merox applications developed by UOP for the control of mercaptans in hydrocarbon streams [3]. The process is based on the ability of a metal chelate, i.e., sulfonated cobalt phthalocyanine (CoPcS), to catalyze the oxidation of mercaptans to disulfides in alkaline medium by oxidation with air. The mechanism of the reaction can be summarized as [4,5]:



Overall reaction:



It is widely accepted that the above mechanism consists of two major steps. In the first step, a base catalyst promotes formation of the

mercaptide anion. In the second step, the mercaptide is converted to disulfide by the formation of a ternary complex involving CoPcS, mercaptide anion and molecular oxygen. As a ligand, RS⁻ binds to CoPcS more strongly than RSH, so the first step, in which RSH is converted to RS⁻ by a base, is of primary importance to sweetening [6].

In the Merox process, an aqueous base, such as caustic or ammonia, is employed for this purpose. However, the aqueous bases always give rise to the environmental problem of spent caustic materials [7]. One possible way to solve this problem is to use solid base catalysts.

Christian et al. [12] used the mixture of basic sodium, silicate, active carbon and adhesives as a solid base in the sweetening of kerosene with high acid number. Jiang et al. [4] reported that MgO supported on Al₂O₃ has been impregnated with a methanol solution of CoPcS to obtain MgO/Al₂O₃-CoPcS catalyst, and this has been compared with hydrotalcite-derived Mg-Al mixed oxide (Mg(Al)O). Results have shown that MgO can disperse on the surface of Al₂O₃ as a monolayer and the monolayer dispersion capacity is 0.17 g MgO/g Al₂O₃. The base amount of MgO/Al₂O₃ increases with the loading of MgO on Al₂O₃ and reaches a maximum at the threshold loading; the base strength of MgO/Al₂O₃ is similar to that of Mg(Al)O. On treating jet fuel, MgO/Al₂O₃-CoPcS shows a slightly higher initial conversion than CoPcS/Mg(Al)O and the lifetime of MgO/Al₂O₃-CoPcS is three times as long as that of Mg(Al)O.

NiO/MgO/Al₂O₃-CoPcS is another catalyst for removal of mercaptans. Mei et al. [6] reported that NiO supported on MgO/Al₂O₃ has been impregnated with a methanol solution of CoPcS to obtain NiO/MgO/Al₂O₃-CoPcS catalyst. This catalyst showed a high initial activity and a much longer lifetime than MgO/Al₂O₃-CoPcS. When nickel oxide is doped into the MgO/Al₂O₃ support, more crystal defects are generated, which increases the amount and type of basic sites.

Another solid base catalyst is MgO/ZrO₂-CoPcS. Jiang et al. [8] reported that MgO supported on ZrO₂ has been impregnated with a methanol solution of CoPcS to obtain MgO/ZrO₂-CoPcS. This

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catalyst demonstrates a very good initial activity of mercaptan oxidation but its stability needs to be improved.

Prakhov et al. [9] supported CoPc on SiO₂ and ZnO by the precipitation method. The results showed that the activity of CoPc/ZnO is greater than for CoPc/SiO₂.

After comparing the various solid bases, it seems that alumina-supported basic oxide can be a valuable choice for the following reasons [4]:

1. Alumina is a well developed industrial catalyst support and its pore structure can vary over a great range to facilitate the dispersion of CoPcS.

2. Alumina may be helpful in increasing the durability of the catalyst, because the stability of alumina is favorable in resisting water.

3. The strength and amount of basic sites can be adjusted by changing the type of supported basic oxide and its loading amount, respectively.

For these reasons, for the demercaptanization of gasoline in this study, we used alumina modified by alkaline earth metal oxides as a solid base and used these bases with the liquid catalyst LCPs30 which was supplied by Pars Oil and Gas Company and prepared by Axens Company. LCPs30 is a commercial liquid phase catalyst that is used in demercaptanization process. As indicated in section 3.1, the main part of this type of catalyst is cobalt phthalocyanine. The other types of commercial catalysts used in this process are in solid forms. Then LCPs30 has been selected as a source of CoPc that can be converted to solid form using solid supports. In this regard we can examine effect of supports on activity of commercial type of cobalt phthalocyanine in the demercaptanization reaction.

EXPERIMENTAL

1. Preparation

1-1. Modification of Supports

A commercial amorphous Al₂O₃ in powder form (BET surface area 190 m²/g) was used as starting material. MgO/ γ -Al₂O₃ was prepared by impregnating the γ -Al₂O₃ with magnesium nitrate solution, followed by drying overnight at 380 K and calcining at 773 K for 4 h. To determine the effect of other alkaline earth metal oxides (CaO, SrO and BaO), other samples have been prepared. Preparation has followed the above-mentioned method using nitrate salts of Ca, Sr and Ba.

This method was followed by drying overnight at 380 K and calcining at 773 K or 1,023 K for 4 h.

1-2. Preparation of Sweetening Catalysts

The catalysts used in this work were prepared by evaporative impregnation of MgO/Al₂O₃, CaO/Al₂O₃, BaO/Al₂O₃ or SrO/Al₂O₃ with a methanol solution of LCPs30 catalyst, and then they were dried in a vacuum at ambient temperature. A scheme for the impregnation preparation is illustrated in Fig. 1.

2. Characterization

2-1. Fourier-transform Infrared Spectrophotometry

The structure of the LCPs30 catalyst was studied by means of a Shimadzu-8400S Fourier-transform infrared (FT-IR) spectrophotometer.

2-2. X-ray Diffraction

The XRD patterns of all of the calcined samples were recorded on a Philips PW-1800 X-ray diffractometer using Cu-K α radiation

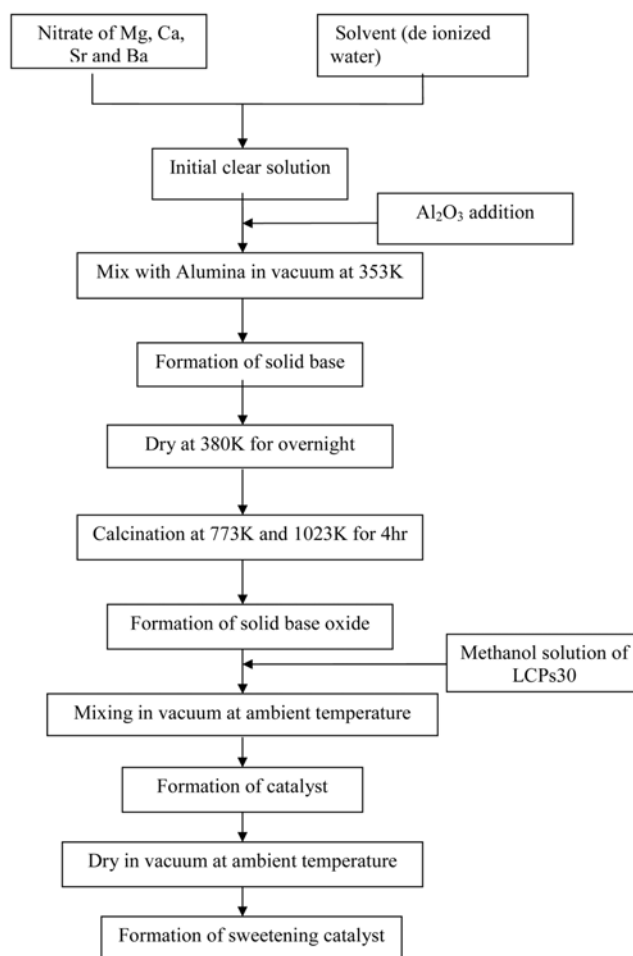


Fig. 1. The preparation scheme for the solid base oxide catalysts by an impregnation process.

($\lambda=1.5406 \text{ \AA}$) at 40 kV and 30 mA to determine the crystalline phases present and to calculate the lattice parameters. Scattering intensities were measured over an angular range of $4^\circ < \theta < 80^\circ$ for all of the samples with a step size (2θ) of 0.03° and a count time of 2 s per step. The diffraction spectra were indexed by comparison with the JCPDS files (Joint Committee on Powder Diffraction Standards).

2-3. Scanning Electron Microscopy and Energy Dispersive Spectrometry

The morphologies of the calcined catalysts prepared at different temperatures (773 °C and 1,023 °C) were studied by scanning electron microscopy (SEM) using a Philips XL30 microscope operating at an accelerating voltage of 30 kV, with a working distance (WD) between 10 and 13 mm and magnification values in the range 100-100,000 \times . SEM was used in the back-scattered electron (BSED) and secondary electron detector (SED) modes to determine the chemical compositions of the crystalline phases, and apparatus-coupled energy-dispersive spectroscopy (EDS) was carried out using an EDS DX-4 analysis system. A very improve the conductivity of the sample.

2-4. Specific Surface Area (BET)

BET specific surface areas (SSAs) were measured by N₂ adsorption at 77 K using a Micromeritics Flow-sorb apparatus, the instrument being operated in single-point mode. Before analysis, the samples were degassed for 2 h at 150 °C.

2-5. Temperature-programmed Desorption (TPD)

This method is used to measure the number and base strengths of sites found on solid base catalysts. The samples were pre-treated at 673 K for 1 h in dry air flow (40 ml/min), and cooled to room temperature, then exposed to pure CO₂ for 1 h. After purging of the catalyst with air for 15 min, the TPD test was run at a heating rate of 283 K/min from room temperature to 673 K. A thermal conductance detector (TCD) detected the desorbed CO₂.

3. Test of Catalytic Activity for Mercaptan Oxidation of Gasoline

A 2 g aliquot of catalyst was added to 50 ml of the feed in a glass reactor, which was operated at 323 K and atmospheric pressure. The feed was gasoline from the Tehran refinery. The mixture was stirred vigorously and the resulting mercaptan level was determined according to UOP-163 method [10].

RESULTS AND DISCUSSION

1. Characterization of Samples

Before the detailed study on the alkaline earth metal oxides on

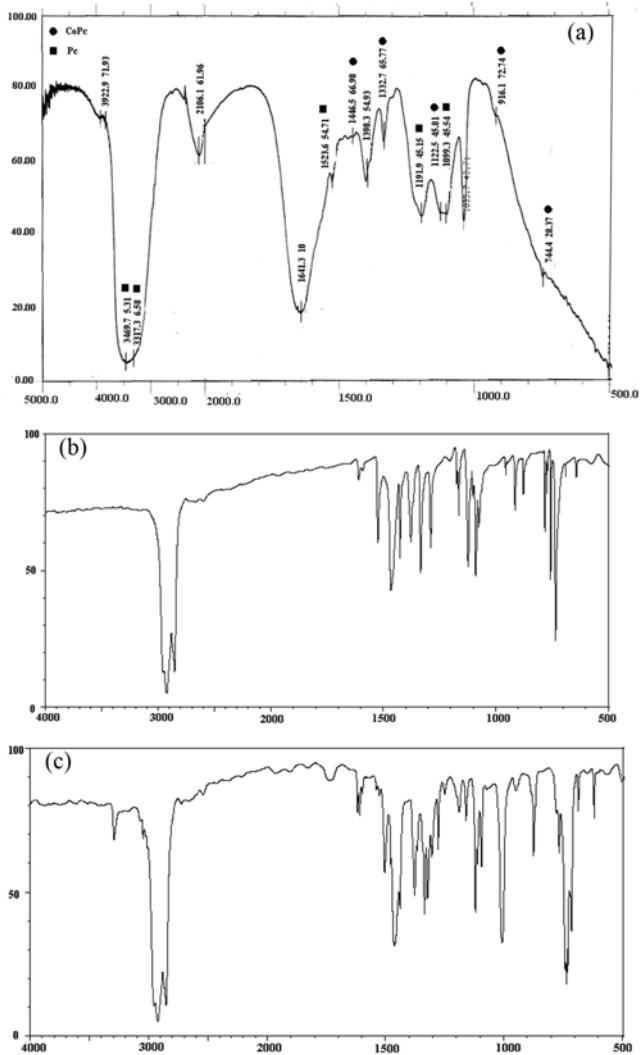


Fig. 2. IR spectra of (a) LCPs30 catalyst, (b) cobalt phthalocyanine [13], and (c) phthalocyanine[13].

Al₂O₃ supported LCPs30 catalyst, the LCPs30 catalyst was studied with FT-IR spectra to determine the ingredients of this catalyst. Fig. 2 shows the corresponding FT-IR spectra of LCPs30 and standard spectra of cobalt phthalocyanine and phthalocyanine [13]. Comparison of this figure with FT-IR of CoPc and Pc indicates that cobalt phthalocyanine and phthalocyanine are present in this catalyst. This figure indicates that phthalocyanine and cobalt phthalocyanine are present in this catalyst. It can be concluded that LCPs30 can be used instead of cobalt phthalocyanine tetrasulfonate in this process. Furthermore, these results are in agreement with the Axens proposal

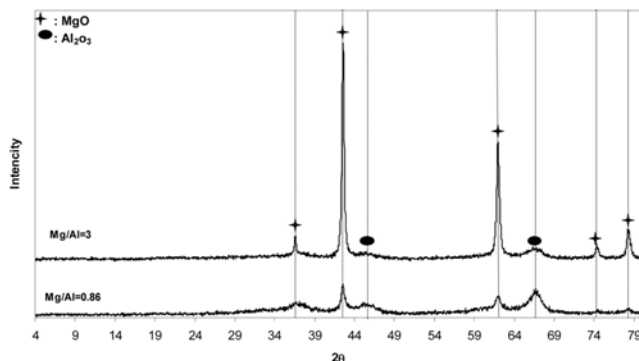


Fig. 3. XRD patterns of MgO/Al₂O₃-LCPs30 with different Mg/Al mole ratios.

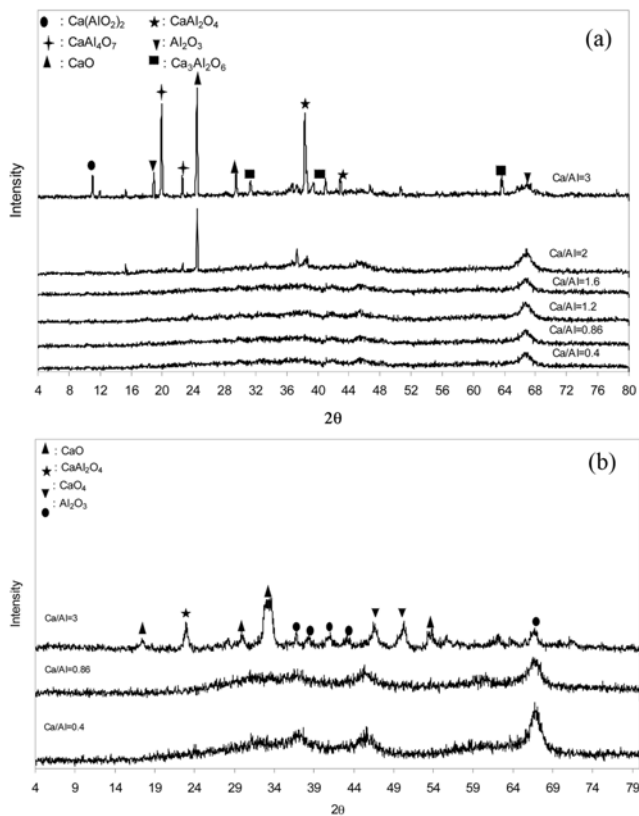


Fig. 4. XRD patterns of CaO/Al₂O₃-LCPs30 with different Ca/Al mole ratios (T=773 °K); (b) XRD patterns of CaO/Al₂O₃-LCPs30 with different Ca/Al mole ratios (T=1,023 °K).

for Pars Oil and Gas Company.

As shown in Fig. 3, the XRD patterns of MgO/Al₂O₃-LCPs30 catalysts showed mainly the characteristic peaks of MgO. The peak intensities of the crystalline MgO increased with the increase in Mg/Al mole ratios. The XRD patterns indicated that catalysts with different Mg/Al mole ratios have the same crystal structure.

XRD patterns of the CaO/Al₂O₃ calcined at 773 K and 1,023 K are shown in Fig. 4(a) and 4(b). To determine the detailed structure of the calcium modified Al₂O₃ under this calcination condition, these samples have been prepared with different mole ratios of Ca/Al. The XRD patterns in Fig. 4(a) indicate that Ca(Al)O, CaO and Al₂O₃ are formed at a calcination temperature of 773 K, for different ratios of Ca/Al. As indicated in this figure, most calcium added to the samples is in the form of calcium aluminates, and calcium oxide formation, which can increase the basic strength, is limited. So calcium present on the structure with aluminum oxide can decrease the basic strength. By increasing the calcination temperature up to 1,023 K (Fig. 4(b)), the diffraction lines are attributed to CaO, CaO₄ and Al₂O₃. Comparing these two figures shows that the higher calcination temperature is suitable for the formation of calcium oxides. Under these conditions, most calcium is present in the oxide forms and the basic strength of these samples is higher. Referring to Fig. 4(a) and 4(b), the XRD peak intensity increases with the increase in Ca/Al mol ratio, which indicates higher basic strength of the samples.

The graph in Fig. 5(a) reveals that, at a calcination temperature of 773 K, strontium oxides are not formed and strontium nitrate peaks

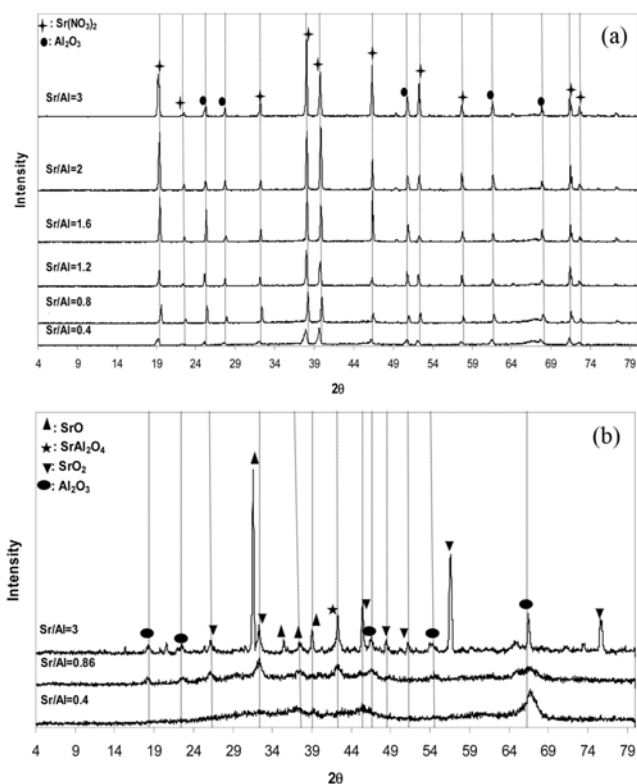


Fig. 5. XRD patterns of SrO/Al₂O₃. (a) XRD patterns of SrO/Al₂O₃-LCPs30 with different Sr/Al mole ratios (T=773 °K); (b) XRD patterns of SrO/Al₂O₃-LCPs30 with different Sr/Al mole ratios (T=1,023 °K).

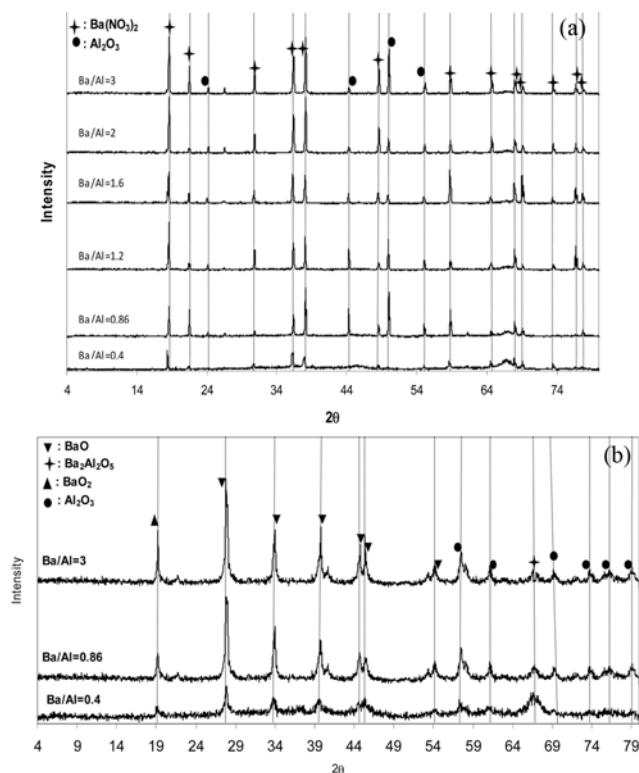


Fig. 6. XRD patterns of BaO/Al₂O₃. (a) XRD patterns of BaO/Al₂O₃-LCPs30 with different Sr/Al mole ratios (T=773 °K); (b) XRD patterns of BaO/Al₂O₃-LCPs30 with different Sr/Al mole ratios (T=1,023 °K).

are observed, whereas at a calcination temperature of 1,023 K, strontium base oxides (SrO, SrO₂) are formed (Fig. 5(b)). Comparing these two figures shows that peak intensities increase with increasing Sr/Al mol ratio, and it can be concluded that the basic strength of the samples calcined at 773 K is less than the basic strength of samples calcined at 1,023 K, because strontium oxides which can increase basic strength are not present in these samples. So a calcination temperature of 1,023 K is the right temperature for the formation of strontium oxides.

The graphs in Fig. 6(a) and 6(b) show that the XRD patterns for BaO/Al₂O₃ at calcination temperatures of 773 K and 1,023 K are the same as for strontium base oxides, so a calcination temperature of 1,023 K is suitable for the formation of barium oxides.

As indicated above, 773 K is not a sufficient condition for the decomposition of Sr and Ba nitrates, and at this temperature the base oxides of Sr and Ba, which can increase basic strength, are not present. So the formation of alkaline earth metal oxides can be important to increase the activity of the catalysts. This evidence has been shown in activity test results.

Therefore, it can be concluded that the calcination temperature increases with increasing atomic number of the alkaline earth metal, so magnesium oxide is formed at 773 K and other alkaline earth metal oxides (CaO, SrO and BaO) are formed at 1,023 K.

Fig. 7 shows scanning electron micrographs (SEM) of samples calcined at 773 K. According to Fig. 7(a)-(e), at 773 K, MgO is dispersed on alumina and other alkaline earth metal oxides are not observed on alumina. However, basic oxides of Ca, Sr and Ba are dispersed on

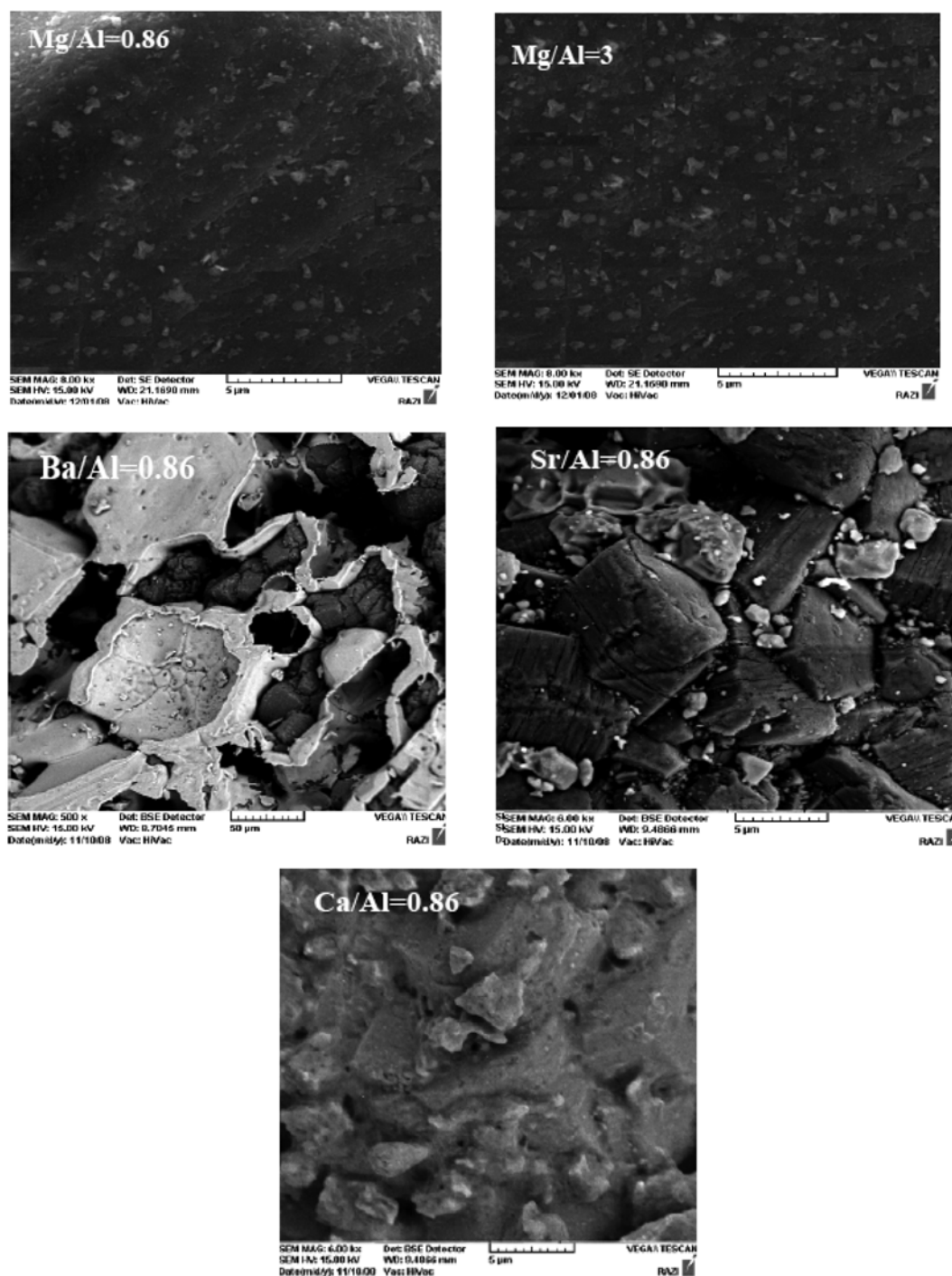


Fig. 7. SEM results at 773 K and 4 hr.

aluminum oxide at 1,023 K (Fig. 8). Furthermore, for MgO at 773 K and other base oxides at 1,023 K, the size of the particles is smaller and their dispersion is better. Also, the size and number of particles increase with increasing Mg/Al, Ca/Al, Sr/Al and Ba/Al mole ratio.

Energy-dispersive X-ray spectroscopy (EDS) coupled with SEM measurements was carried out at different points on some samples calcined at 773 K and 1,023 K to determine the mean element proportions of the samples and ascertain the homogeneity of the preparation for catalysts. Referring to Fig. 9, a comparison between theo-

retical calculations and the results of EDS analysis demonstrated the formation of homogeneous samples.

The basicity of the some samples was characterized by temperature programmed desorption (TPD). TPD results showed that MgO/Al₂O₃ with Mg/Al=3 have two peaks at 456 K and 1,028 K (Fig. 10). Also, CO₂-TPD plots of the BaO/Al₂O₃ with Ba/Al=0.4, 0.86 (Calcined at 1,023 K) are shown in Fig. 11. The CO₂-TPD plots indicate that these catalysts had different amounts of basic sites on their surfaces. These plots have two basic sites corresponding to the

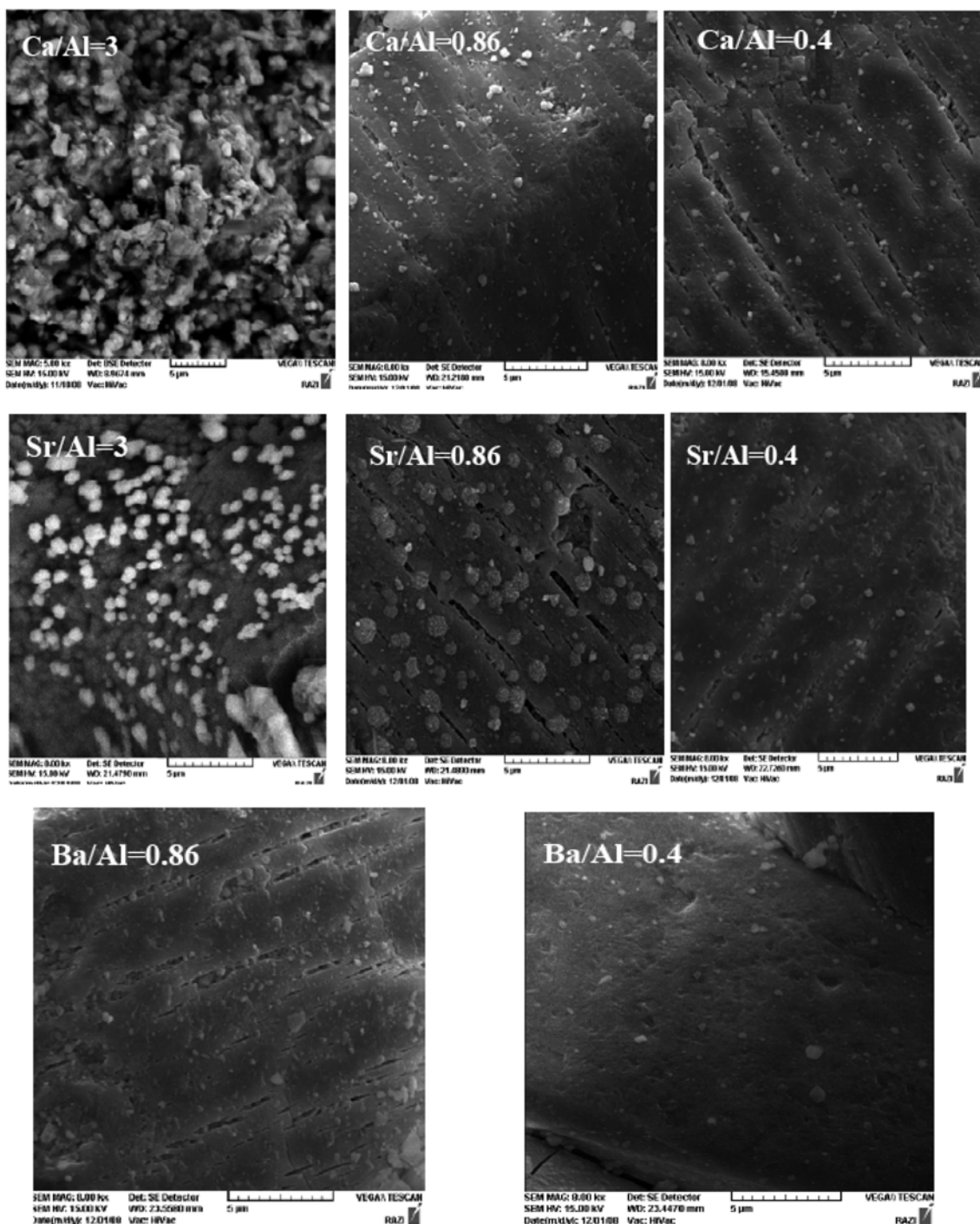


Fig. 8. Scanning electron microscopy for solid base oxide catalysts of Ca, Sr and Ba at 1,023 K.

452 K and 905 K, and the peak areas increase when Ba/Al mole ratios increase. According to these plots, the amount of basic sites increases by increasing Ba/Al mole ratios.

Specific surface area of the catalysts was computed according to the BET method, and this is summarized in Table 1. The results of BET measurements showed that increasing base oxide loading in the samples resulted in a smaller, surface area of catalysts.

According to the XRD results, the calcination temperature of MgO is less than for the other oxides. An increase in calcination temper-

ature results in sintering, which causes a decrease in porosity and particle accumulation, so the surface area will decrease. Therefore, the surface area of MgO is greater than for the other alkaline earth metal oxides. Furthermore, in a specific set of salt nitrate samples, the surface areas of the samples decrease with increasing X/Al mole ratio (X=Mg, Ca, Sr, Ba) because the alkaline earth metals promote the sintering effect and decrease the surface area.

2. Performance of Mercaptan Oxidation of Gasoline

Figs. 12 and 13 show the conversion of mercaptan and remaining

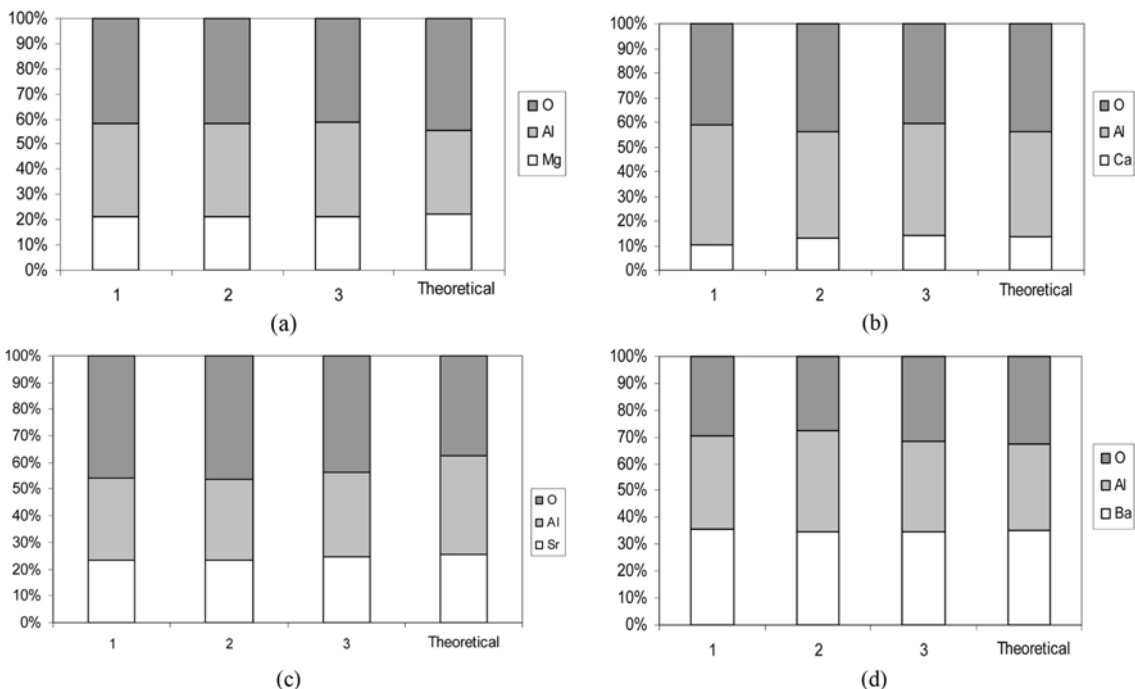


Fig. 9. Al, O, Mg, Ca, Ba and Sr distribution observed at different points along the samples by EDS. (a) $\text{MgO}/\text{Al}_2\text{O}_3$ ($\text{Mg}/\text{Al}=0.86$) calcination at 773 K, 4 hr; (b) $\text{CaO}/\text{Al}_2\text{O}_3$ calcination ($\text{Ca}/\text{Al}=0.86$) at 1,023 K, 4 hr; (c) $\text{SrO}/\text{Al}_2\text{O}_3$ calcination ($\text{Sr}/\text{Al}=0.86$) at 1,023 K, 4 hr; (d) $\text{BaO}/\text{Al}_2\text{O}_3$ calcination ($\text{Ba}/\text{Al}=0.86$) at 1,023 K, 4 hr.

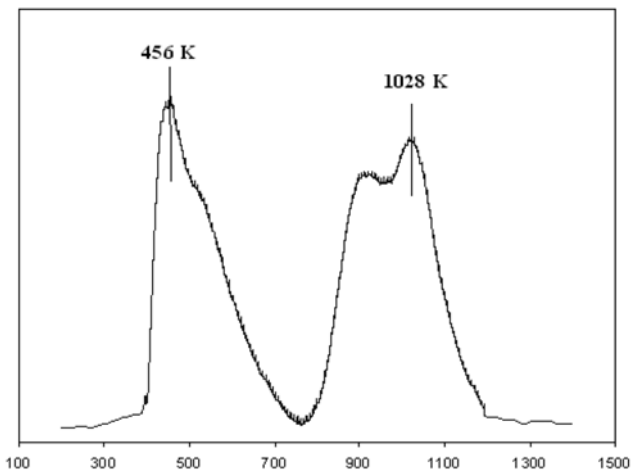


Fig. 10. CO_2 -TPD plots of $\text{MgO}/\text{Al}_2\text{O}_3$ ($\text{Mg}/\text{Al}=3$).

mercaptan as a function of mole ratio by catalysts, respectively. For $\text{MgO}/\text{Al}_2\text{O}_3$ ($T_{\text{cal}}=773$ K), additional loading from 0.86 to 3 results in increasing the mercaptan conversion from 95% to 98%. For other catalysts at the calcination temperature of 1,023 K, the mercaptan conversion increases with increasing mole ratio from 0.4 to 3. A comparison of the graphs indicates that mercaptan conversion of Ba is more than for Sr and Ca, and Ca has the minimum conversion. In the range of 0.4 to 3, the conversions of $\text{CaO}/\text{Al}_2\text{O}_3$, $\text{SrO}/\text{Al}_2\text{O}_3$ and $\text{BaO}/\text{Al}_2\text{O}_3$ increase from 38% to 79%, 63% to 90% and 63% to 95%, respectively.

The results of reactions of samples of Ca, Sr and Ba calcined at 773 K are presented in Fig. 14. As indicated, the conversion of mercaptans is related to mole ratio. The trend in this figure is not similar

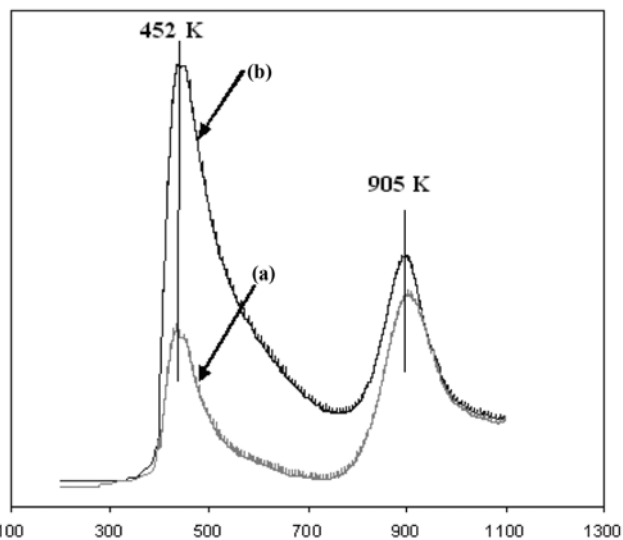


Fig. 11. CO_2 -TPD plots of $\text{BaO}/\text{Al}_2\text{O}_3$, (a) $\text{Ba}/\text{Al}=0.4$, (b) $\text{Ba}/\text{Al}=0.86$.

to that in Fig. 10 and this trend is not stable, because the base oxides are not formed at 773 K and the basic strengths of these samples are limited.

Referring to the above results and the results of the XRD patterns, it can be concluded that formation of base oxides can be important for increasing the activity of catalysts. In addition, calcination temperature of magnesium is less than for the other alkaline earth metals, so the surface area and conversion of $\text{MgO}/\text{Al}_2\text{O}_3$ -LCPs30 are greater than for the others. Moreover, it is found that in other base oxide catalysts, calcined at the same temperature, the conversion is increased with increasing atomic number of alkaline earth metal, because the

Table 1. Specific surface area of various samples

Sample	T _{cal} (K)	Mole ratio	BET (g/m ²)
MgO/Y-Al ₂ O ₃	773	0.86	150
MgO/Y-Al ₂ O ₃	773	3	36.06
CaO/Y-Al ₂ O ₃	1023	0.4	60.01
CaO/Y-Al ₂ O ₃	1023	0.86	18.49
CaO/Y-Al ₂ O ₃	1023	3	5.83
SrO/Y-Al ₂ O ₃	1023	0.4	74.82
SrO/Y-Al ₂ O ₃	1023	0.86	14.82
SrO/Y-Al ₂ O ₃	1023	3	6.14
BaO/Y-Al ₂ O ₃	1023	0.4	26.99
BaO/Y-Al ₂ O ₃	1023	0.86	21.62
BaO/Y-Al ₂ O ₃	1023	3	5.41

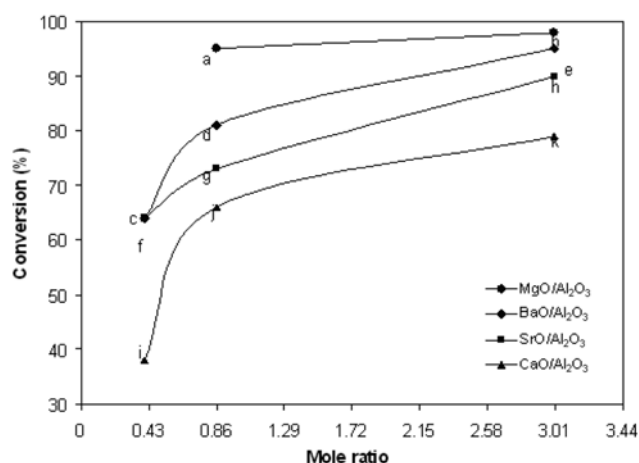


Fig. 12. Mercaptan conversion. (a) Mg/Al=0.86; (b) Mg/Al=3; (c) Ba/Al=0.4; (d) Ba/Al=0.86; (e) Ba/Al=3; (f) Ca/Al=0.4; (g) Ca/Al=0.86; (h) Ca/Al=3; (i) Sr/Al=0.4; (j) Sr/Al=0.86; (k) Sr/Al=3.

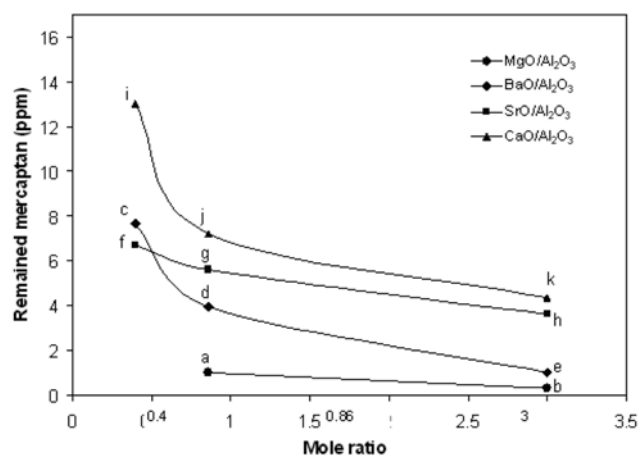


Fig. 13. Remaining mercaptan. (a) Mg/Al=0.86; (b) Mg/Al=3; (c) Ba/Al=0.4; (d) Ba/Al=0.86; (e) Ba/Al=3; (f) Ca/Al=0.4; (g) Ca/Al=0.86; (h) Ca/Al=3; (i) Sr/Al=0.4; (j) Sr/Al=0.86; (k) Sr/Al=3.

basicity increases [11]. Furthermore, in a specific set of salt nitrate samples, the conversion of mercaptans increases with increasing

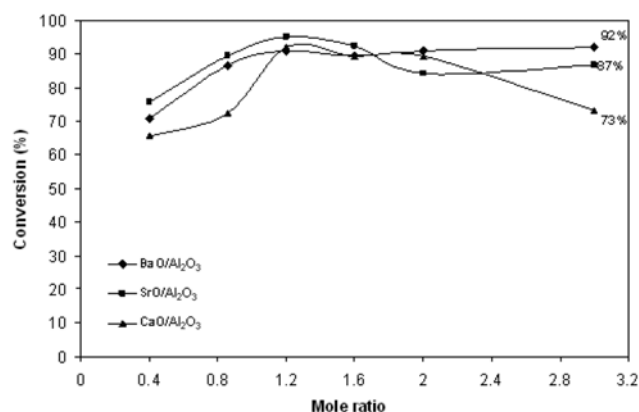


Fig. 14. Conversion of mercaptan for samples calcined at 773 K and 4 hr.

X/Al (X=Mg, Ca, Sr and Ba) mole ratio, because mercaptan oxidation is a quick reaction and the secondary product increases with increasing surface area; thus samples with lower surface area have a better conversion. It will be noted that, with mole ratio increasing from 0.4 to 0.86, the increase in conversion is considerable, whereas this trend is continued much more slowly for loading from 0.86 to 3. These results indicate that MgO has the highest conversion compared to the other base oxides and a high mole ratio of catalyst must be used to reach the high conversion in base oxides of Ba, Sr and Ca.

CONCLUSION

It can be concluded that the alkaline earth metal oxides are formed at 1,023 K, excluding MgO, which is formed at 773 K. In addition, the basicity of catalysts and the number and size of solid base oxides increase with increasing X/Al mole ratios (X=Mg, Ca, Sr, Ba). Also, the XRD patterns indicate that, for all alkaline earth metal oxides, the catalysts with different mole ratios have the same crystal structure. The TPD results indicated that increasing base oxide loading in the samples could lead to the increase of base amounts on the surfaces. Furthermore, it is found that the surface area of MgO is greater than for the other alkaline earth metal oxides, and in a specific set of salt nitrate samples, the surface areas of catalysts decrease with increasing X/Al mole ratio (X=Mg, Ca, Sr, Ba). MgO/Al₂O₃-LcPs30 has the highest surface area and conversion compared to the other base oxides, and in the other base oxide catalysts calcined at the same temperature (1,023 K), the conversion is raised with increasing atomic number of the alkaline earth metal. The results show that, in a specific set of salt nitrate samples, the conversion of mercaptans increases with increasing X/Al (X=Mg, Ca, Sr and Ba) mole ratio.

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