Microwave catalytic effects in highly effective direct decomposition of NO and H_2S by microwave catalysis

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1. Introduction (11-point boldface)

The direct catalytic decomposition of NO into N_2 and O_2 is recognized as the most ideal and economical way for NO removal, while the high NO conversion and N_2 selectivity is still a great challenge at low temperature under excess oxygen. Simultaneously, the direct decomposition of H_2S into H_2 and S has attracted increasing attention because it can simultaneously recover valuable H_2 and elemental sulfur from a highly toxic waste gas. However, the thermal equilibrium limitation in this reaction presents a great challenge to direct decomposition of H_2S with high efficiency.

On the other hand, the use of microwave irradiation to increase the rate of chemical reactions has attracted much attention recently in nearly all fields of chemistry due to substantial enhancements in reaction rates. However, the intrinsic nature of the effects of microwave irradiation on chemical reactions remains unclear.

We have recently reported a highly effective approach for direct decomposition of NO and direct decomposition of H_2S into H_2 and S that can be achieved by microwave catalysis.[1-6] We attempt to open a novel approach for direct decomposition of NO and direct decomposition of H_2S reaction, and reveal the microwave catalytic effects in heterogeneous catalytic reactions.[1-7]

2. Experimental (or Theoretical)

We have devised a new multi-mode microwave reactor for heterogeneous gas-solid catalytic reactions. The direct decomposition of NO and direct decomposition of H_2S via microwave catalysis have been recently investigated in our laboratories using the parallel microwave catalytic reaction mode (MCRM) and conventional reaction mode (CRM). More details about experimental can be found in our previous study.[1-6] For NO decomposition reaction, a series of microwave catalysts, such as MeO_x-Cu-ZSM-5, $BaMn_{1-x}Mg_xO_3$ and $BaBO_3$ (B=Mn,Co,Fe) were studied. For H_2S decomposition reaction, MeS-based microwave catalysts were investigated.

3. Results and discussion

Figure 1a shows the illustration of microwave direct catalytic effect for the direct NO decomposition by microwave catalysis. Surprisingly, even at 100 ℃ (a greatly low reaction temperature for NO decomposition), NO conversion can achieve 43.2% for $BaMnO_3$ and 38.4% for $BaCoO_3$ in the MCRM. Importantly, the best NO conversion is highly up to 93.7% for $BaMnO_3$ at 300 ℃ and 99.9% for $BaCoO_3$ at 250 ℃. Comparatively, in the CRM, the highest NO conversion are only 45.4% for $BaMnO_3$, and 46.8% for $BaCoO_3$. Obviously, the catalytic activity can be remarkably enhanced through microwave catalysis for NO decomposition. Moreover, Ea' for $BaMnO_3$ and $BaCoO_3$ are respectively decrease from 194.5 and 153.7 kJ/mol in the CRM to as low as 33.4 and 13.7 46.7kJ/mol in the MCRM, showing an excellent microwave catalytic effect under microwave irradiation.[4]

It is surprised that oxygen concentrations (0-10%) do not inhibit the catalytic NO decomposition reaction in the MCRM. Moreover, N_2 selectivity is more than 99.9% at low temperature of 250 ℃ in the MCRM (Figure 1b). It was found a significant microwave selective effect to oxygen inhibition removal.

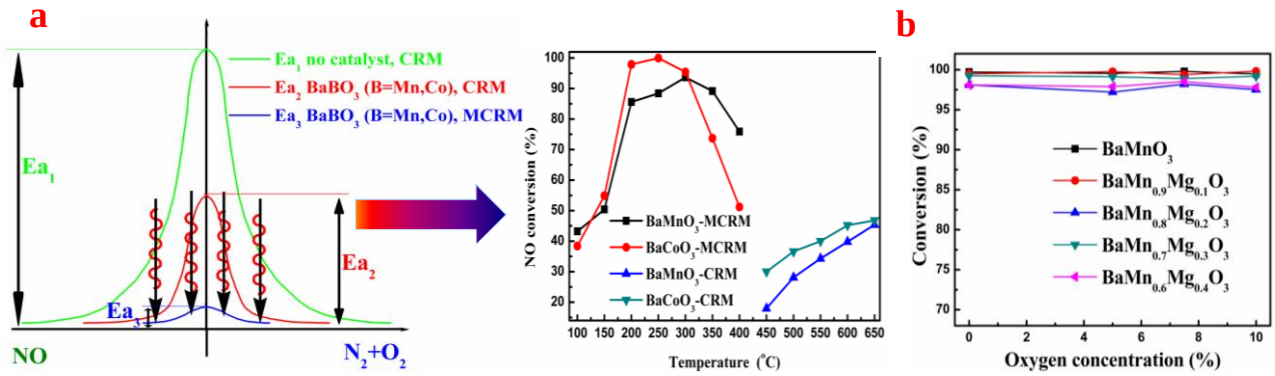

Figure 1. (a) Illustration of microwave direct catalytic effect for the direct NO decomposition by microwave catalysis, (b) oxygen inhibition removal by microwave selective catalytic effect under microwave irradiation

Figure 2a displays the illustration of microwave selective catalytic effect for the direct H_2S decomposition by microwave catalysis. It is noteworthy that H_2S equilibrium conversions are relatively low for such a thermodynamically unfavorable reaction (eg. 19.3% at 825 ℃). Surprisingly, the H_2S conversion under microwave irradiation is much higher than the equilibrium conversion in the conventional thermal reaction. For NiS/γ-Al_2O_3/$BaMn_{0.2}Cu_{0.8}O_3$, the H_2S conversion at 650 °C has risen from 6.3% of equilibrium conversion to 49.9% under MW irradiation. For CoS/γ-Al_2O_3/$BaMn_{0.2}Cu_{0.8}O_3$, the H_2S conversion at 788 °C has risen from 15.95% of equilibrium conversion to 80.33%. These results indicate that H_2S conversions under microwave irradiation are greatly higher than that of the equilibrium conversion. It was found that the microwave irradiation exhibited selective catalytic effect, which can break the chemical equilibrium of gas-solid phase continuous flow catalytic H_2S decomposition process over MeS-based catalysts under microwave irradiation (Figure 2b).

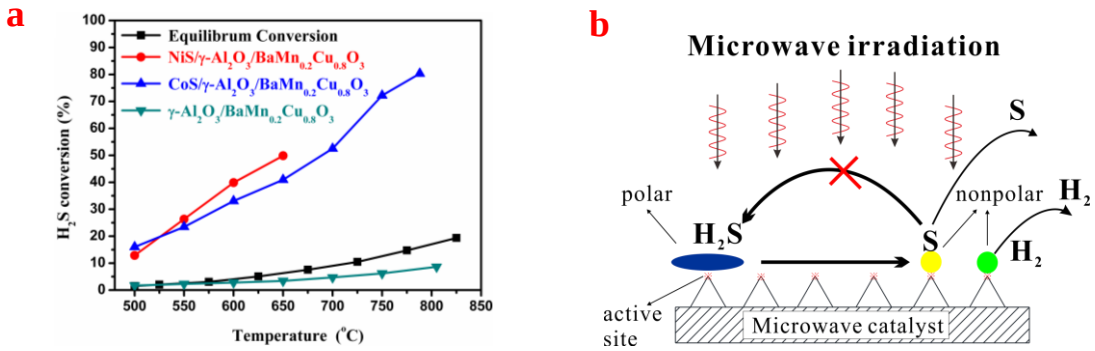

Figure 2. (a) H_2S conversion versus reaction temperature for NiS/γ-Al_2O_3/$BaMn_{0.2}Cu_{0.8}O_3$, (b) Illustration of microwave selective catalytic effect for the direct H_2S decomposition by microwave catalysis

4. Conclusions

An attractive and environmental friendly process for NO_x emission control and direct decomposition of H_2S into H_2 and S has been exploited. NO conversion and H_2S conversion is highly up to 99.9% at 250 ℃ and 80.33 % at 788 ℃. Microwave selective catalytic effect can remove oxygen inhibition for NO decomposition, and can break the chemical equilibrium of the H_2S decomposition reaction.

References

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