

Kinetics of in-direct and direct sulfation of limestone

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The desulfurization process has been considered to reduce emissions of SO₂ from industrial facilities such as coal power plant, cement plant and steel mill. The desulfurization process of limestone takes place with two-step process. First, calcination of limestone occurs at high temperature furnace. The calcination process makes limestone decompose to CaO. After calcination, SO₂ molecules is adsorbed onto pores of the calcined limestone (CaO). This two-step process is called the in-direct sulfation which are used to existing FGD (Flue gas desulfurization) system. If CO₂ partial pressure in the system is higher than equilibrium CO₂ pressure over limestone, it prevents a calcination (decomposition) of limestone. So adsorption reaction between limestone and SO₂ molecules takes place directly at the uncalcined state. This one-step process is called the direct sulfation. Direct sulfation of limestone usually have been known to occur for desulfurization by pressurized fluid-bed combustion (PFBC) or oxy-fuel combustion system capturing CO₂.

The experiments were performed with the thermogravimetric analyzer (TGA). Two carrier gases were supplied to experimental setup to compare direct sulfation with in-direct sulfation. For a direct sulfation, a carrier gas was composed of 80% CO₂ and 20% O₂ and a carrier gas of 100% air was used for an in-direct sulfation. Both carrier gases contain 3000ppm SO₂. The weight change of samples was measured in order to infer reaction of samples.

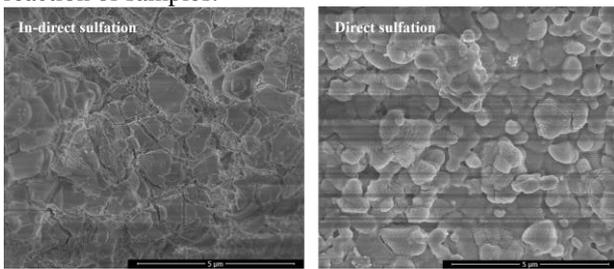


Figure 1. SEM images of surface of limestone samples reacted under in-direct and direct sulfation conditions

The SEM images of the surface of limestone samples are represented in Figure 1. There are cracks like a valley at surface of limestone samples reacted under the in-direct sulfation condition. When samples begin a calcination, cracks on surface of them are created by outflow of CO₂ molecules and then SO₂ molecules can be supplied through the cracks to adsorb onto the surface of the calcined limestone. The size of these cracks is relatively large right after calcination but the width of cracks become thin gradually as in-direct sulfation proceeds. Since thickness of cracks SO₂

molecules pass through become main route supplying SO₂ molecules become thinner during in-direct sulfation process, efficiency of sulfation decreases sharply when cracks are plugged by sintering process as sulfation progresses. Micro-pores can be observed at the surface of limestone samples right after a calcination during the direct sulfation process, because the partial pressure of CO₂ above the limestone particles prevents the decomposition of CO₂ molecules. The diffusion mechanism under the direct sulfation process is pore diffusion in the particle and product through micro-pore made by decomposition of CO₂ molecules, while SO₂ molecules are diffused through cracks between grains under in-direct sulfation process.

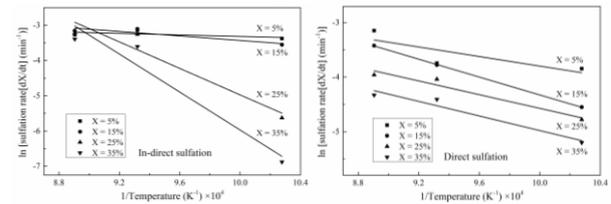


Figure 2. Arrhenius plots of in-direct sulfation (left) and direct sulfation (right)

Table 1. Apparent activation energy of in-direct and direct sulfation.

Sulfation degree	Apparent activation energy (kJ/mol)	
	In-direct sulfation	Direct sulfation
0.05	8.802	30.69
0.15	26.59	49.53
0.25	136.1	77.42
0.35	223.8	32.75

Table 1 shows the values of the apparent activation energy of in-direct and direct sulfation which are calculated by the Arrhenius plots (Figure 2). The values of in-direct sulfation increased drastically as the sulfation degree increases but these of direct sulfation didn't change considerably although the sulfation degree increases.

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