

CHAPTER II

LITERATURE REVIEW

2.1 NO_x

During the combustion at temperatures higher than about 1,000°C, nitrogen compounds can be formed from two sources: (1) from the molecular nitrogen in the combustion air (N₂), and (2) from nitrogen, which is contained in some fuels. They are nitric oxide (NO), nitrogen dioxide (NO₂), and nitrous oxide (N₂O). These are commonly referred to as NO_x. Of the NO_x emissions, about 95 % is NO, whereas the fraction of NO₂ and N₂O remains less than 5 %.

The well-known harmful effects of NO_x to the environment are: it is the acid rain causing substances, creates the photochemical smog and ozone in big cities, and it (i.e., N₂O) is identified as a greenhouse gases that participates in the changing of global climate.

NO_x, typically, can be formed in the following three ways: (1) Thermal NO_x, (2) Prompt NO_x, and (3) Fuel NO_x.

1. Thermal NO_x:

This NO_x generation mechanism highly depends on the temperature. It is the main source of NO_x in the fuel-rich combustion at high temperatures. NO_x formed in most of coal-fired units are thermal NO_x and fuel NO_x, which represent about 25% and 75%, respectively. But for the combustion devices that operate at very high temperatures, NO_x generation can be considerably referred to thermal NO_x than fuel NO_x. Temperature, time, and mixing are the primarily factors that affect the quantity of thermal NO_x formation (Glarborg *et al.*, 2001).

2. Prompt NO_x:

This kind of NO_x formation can be occurred in hydrocarbon based gaseous flames where the maximum temperature is about 1300°C. And its principle reaction is the reactions of hydrocarbon fuel derived radicals with N₂ and O₂.

3. Fuel NO_x:

This type of NO_x formation occurs when nitrogen in the fuel reacts with O₂ to form NO. It is an important source of NO_x generated from the combustion of

fossil-based solid fuel and biomass fuels. The reaction contributes over 80% of the total NO in a coal or biomass combustion system. It does not highly depend on temperature.

A short summary of the mechanisms for NO_x formation is given in Table 2.1.

Table 2.1 Summary of NO and NO₂ formation (Kilpinen, 2000)

n:o	Reaction
1	Thermal NO $N_2 + O \rightarrow NO + N$ $N + O_2 \rightarrow NO + O$ $N + OH \rightarrow NO + H$
2	Prompt NO $N_2 + CH \rightarrow HCN + N$ $HCN \xrightarrow{+O} NCO \xrightarrow{+H} NH \xrightarrow{-H} N \xrightarrow{+O_2, +OH} NO$
3	Formation via N ₂ O intermediate $O + N_2 + M \rightarrow N_2O + M$ $N_2O + O \rightarrow 2NO$

In Thailand, there is some legislation for gas emission. The example of NO_x emission standard for municipal waste incinerators is shown in Table 2.2.

Table 2.2 Emission standards for municipal waste incinerators (Ministry of Science, Technology and Environment, Thailand, 1997)

Pollutants	Maximum Standards*	
	Size	
	1-50 ton/day	More than 50 ton/day
1. Total Suspended Particulate (mg/m ³)	400	120
2. Sulfur Dioxide (SO ₂)(ppm)	30	30
3. Oxides of Nitrogen (NO _x as NO ₂)(ppm)	250	180
4. Opacity (%)	20	10
5. HCl (ppm)	136	25
6. Dioxin(ng/m ³)	30	30

*At reference condition of 25 °C at 1 atm in excess air at 50% or excess oxygen 7% and dry basis.

2.2 NO_x Control Technologies

The technologies that are the most effective and most widely applied for NO_x control are as follows:

2.2.1 Combustion Control

Combustion control is the NO_x control technologies which are intended to minimize NO_x emissions by (1) lowering the temperature in the combustion zone to suppress NO_x formation, (2) decreasing the oxygen concentration available for NO_x formation in the high temperature zones, and/or (3) creating conditions under which NO_x can be reduced to molecular nitrogen by reacting with hydrocarbon fragments. The technologies include (Zevenhoven and Kilpinen, 2002):

- Low excess air: reducing the available oxygen to the amount only sufficient to oxidize the fuel but not too much to cause the NO_x emissions,
- Over fire air: by diverting combustion air to the over fire ports. The unburned materials leaving the main combustion zone will be burnt by mixing with the over fire air,
- Staged combustion: staging combustion by arranging the inlets of fuel or air to achieve similar effects as over fire air,
- Flue gas recirculation: recirculating the flue gas to the combustion zone to reduce flame temperature and oxygen concentration, and
- Gas reburning: introducing fuel gas to burn in the post combustion zone to generate various types of hydrocarbon fragments which reduce the NO_x formed in the main combustion zone to molecular nitrogen.

In some cases, fuel and/or air staging is achieved directly within the burner and such systems are identified as "low NO_x burners".

2.2.2 Selective Non-Catalytic Reduction (SNCR)

This technology involves injecting reagents such as ammonia or urea in the furnace. The operating temperature is about 1000°C. The NO_x formed during combustion can be reduced to nitrogen by reacting with those reagents.

Typically, the NO_x reduction efficiency of SNCR is about 50%.

2.2.3 Selective Catalytic Reduction (SCR)

This is an end-of-pipe combustion control technology. The reduction of NO_x can be done by the injection of reagents such as ammonia or hydrocarbons to enhance the reaction in the presence of catalysts. The reaction temperature is about between 250°C and 400°C which is suitable for flue gas scrubbing. The NO_x reduction efficiency of this method is about 80% to 90%.

(<http://wlapwww.gov.bc.ca/epd/cpr/policy/elngfb.html#5> accessed on 15/04/2005)

2.3 Selective Catalytic Reduction of NO_x with NH₃

There are many methods for NO_x removal from gas emissions. But the most powerful one is selective catalytic reduction (SCR). If the emission source is stationary, the NO_x reduction with NH₃ is preferentially used, and it can achieve to 90% of NO conversion.

The SCR process is based on the injection of ammonia (NH₃), as a reducing agent, into the flue gas stream at before the zone of a catalyst matrix. Ammonia will react with NO_x (NO and N₂O) to produce nitrogen (N₂) and water (H₂O) as the products. The chemistry is given in Figure 2.1.

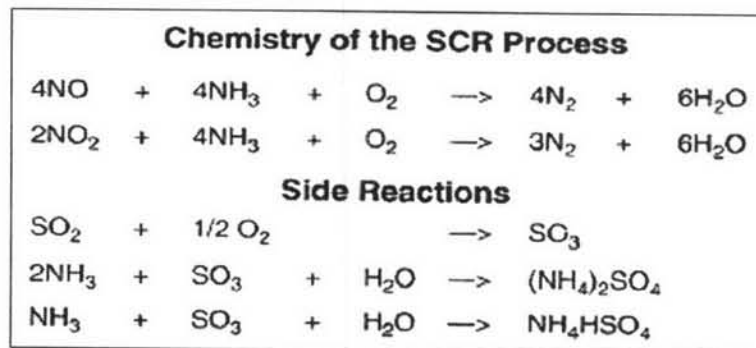


Figure 2.1 Simplified SCR chemistry (Zevenhoven and Kilpinen, 2002).

Because the NH₃/NO_x ratio depends on the oxidation state of NO_x, the either excessive or insufficient NH₃ addition can yield the problem of either of NH₃ or NO_x slips, respectively. To prevent these emissions occurred, the typical NH₃/NO_x ratio is maintained to about 0.8 to 1.0.

Generally, SCR is effective at the low temperatures, but at the higher temperature, NO_x conversion is higher. The operating temperature in SCR reaction depends on the type of the catalyst material, which is typically made from noble metals, including metal oxides such as vanadium pentoxide and titanium dioxide, or zeolite-based materials. For examples, platinum and vanadium catalysts are effective at 450°C whereas the temperature at 600°C is the effective for the ion-exchanged

zeolites. Typically, the effective operating temperature for NO_x reduction is about 250 to 400°C.

2.4 Catalysts for SCR Process

2.4.1 Vanadium-catalysts

In SCR of NO_x by NH_3 , the commercial 7 wt% vanadia on titania catalysts ($\text{V}_2\text{O}_5/\text{TiO}_2$ or $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$) is a preferred choice of industries emitting NO_x . Over $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts, about 67% NO conversion was observed at 350°C (Long and Yang, 1999). In year 2000, they found that VO-TiO₂-PILC (VO^{2+} ion-exchanged TiO_2 – pillared clays) had the maximum activity at 2.1-3.1 wt% vanadium loading, which is slightly higher than the activity of the commercial $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst. In the same year, they also found that the addition of WO_3 to V_2O_5 further increased the activities of the PILC catalysts. In addition, WO_3 can increase the catalyst resistance against chemical deactivation and reduce SO_2 oxidation to SO_3 and NH_3 oxidation. (Long and Yang, 2000)

The disadvantages of this commercial catalyst are: the toxicity of vanadium itself and it catalyzes the oxidation of SO_2 to SO_3 , which can give sulphuric acid corrosion problems downstream at lower temperatures. In addition, in the SCR unit, ammonium sulphates can be formed as the side reaction shown in Figure 2.1. This can result in corrosive deposits in the SCR unit as well as downstream, and also causes catalyst deactivation (Zevenhoven and Kilpinen, 2002). And Solis *et al.* (2003) reported that the vanadia-catalysts had relatively low H_2O tolerance but higher for SO_2 resistance.

2.4.2 Metal-exchanged Zeolite Catalysts

Zeolite is one of the most preferentially used catalyst support in NO_x reduction. To enhance its activities, many types of metal have been added via exchange or impregnation techniques. And the most frequently used metals are Cu, Fe, Ni, and Co known to be active in the low-temperature de NO_x SCR reaction (Marban *et al.*, 2003).

The first metal-exchanged ZSM-5 catalyst of significant interest was Cu/ZSM-5. Iwamoto *et al.* (1991) observed the enhancement of NO_x reduction with the presence of excess oxygen using copper ion-exchanged zeolites. NO_x reduction began at around 300°C and reached a maximum between 400-450°C. Long *et al.* (1998) found that when doped with some metal oxides (i.e., Cu, Fe, Co, Ag, and Ga) on Ti-PILC, Cu-Ti-PILC showed the highest activities at temperatures below 370°C. Salker and Weisweiler (2000) found that Cu/ZSM-5, with co-feeding of water, showed better catalytic activities than Fe/ZSM-5 and Cr/ZSM-5 in NO_x reduction, but it was worse in the case of NH₃ conversion. The reason was that Cu/ZSM-5 allowed both NH₃ and NO_x chemisorption whereas there was no prominent NO_x adsorption detected on Fe/ZSM-5 and Cr/ZSM-5.

In many experiments on Cu-based catalysts, H₂O or SO₂ were not included in the feed. When these components are co-fed into the reactor, NO_x reduction is inhibited. For short duration, the inhibiting effect of H₂O is reversible while extended exposure to water vapor irreversibly deactivates Cu/ZSM-5 catalysts. This effect is accelerated at elevated temperatures (Long *et al.*, 1998, and Salker and Weisweiler, 2000).

Several experiments of NO_x reduction by using Fe/ZSM-5 have been accomplished. Many authors found that Fe/ZSM-5 catalyst was highly active for SCR of NO_x (Heinrich *et al.*, 2001, and Wood *et al.*, 2000). It can achieve nearly to 100% NO conversion at 400-550°C, which is very relatively higher when compared with H-ZSM-5 and the commercial, V₂O₅-WO₃/TiO₂, catalyst (Long and Yang, 2001). Brink *et al.* (2000) found that by using propane as the reductant, 90% N₂O conversion can be achieved at the lower temperature than using methane (350°C and 450°C, respectively). And, they also found that the NO_x reduction increased with increasing pressure.

In many experiments, the mechanism for NO_x reduction on Fe/ZSM-5 has been proposed. Kogel *et al.* (2001) found that NO and NO₂ acted as “co-catalysts” during N₂O decomposition by facilitating the desorption of strongly adsorbed atomic oxygen. Wood *et al.* (2002) prepared Fe/ZSM-5 catalysts using the solid-state exchange method. They found that Fe²⁺ metal sites were more active for N₂O decomposition than the Fe³⁺ ones. Long and Yang (2002) studied about the

mechanism of Fe/ZSM-5 catalyst. They reported that gaseous NH_3 molecules were adsorbed quickly onto Bronsted acid sites on the catalyst forming NH_4^+ ions. And NO molecules were oxidized to NO_2 on Fe^{3+} sites by O_2 , which is a slow reaction. Then, one molecule of NO_2 diffused to two adjacent NH_4^+ ions to form the active complex, $\text{NO}_2(\text{NH}_4^+)_2$, then it subsequently reacted with one molecule of NO to produce N_2 and H_2O . Huang *et al.* (2002) also supported the observations and additionally found that the rate of NO conversion on Fe/ZSM-5 was first-order with respect to NO, zeroth-order with respect to NH_3 and nearly half-order with respect to O_2 , at 260-300°C.

The advantages for Fe-loading over other metal-exchanged zeolites are: it highly increases the catalyst activity, yields only N_2 as the product, and has relatively higher water vapor and SO_2 resistance (Fanson *et al.*, 2003 and Adelman *et al.*, 2002). These statements were supported by Marban *et al.* (2003). They found that at about 5-6 wt% of metal-loading prepared by impregnation method, the catalytic activity order was found to be: $\text{Fe} > \text{Mn} > \text{V} > \text{Cr} > \text{Ni}$. And, they also reported that SO_2 partially deactivated the Mn-, Fe-, and Cr-based catalysts (deactivation order: $\text{Mn} > \text{Fe} > \text{Cr}$) and hardly deactivated the V-based catalysts. Furthermore, H_2O had a reversible inhibitory effect on those catalysts.

Other formulations such as Pt on zeolite-supported catalyst have been proven very efficient for SCR of NO_x . Supported Pt catalysts are active at lower temperatures (150° to 350°C), but they are more prone to N_2O , a strongly greenhouse gas, formation than others (Parvulescu *et al.*, 1998). Fanson *et al.* (2002) found that the role of platinum on Pt/ $\gamma\text{Al}_2\text{O}_3$ was to adsorb O_2 under lean conditions and reducing gases under rich condition.

Palomares *et al.* (2000) studied NO reduction on Cu/IM5 and found that Cu/IM5 was more active and hydrothermally more stable than Cu/ZSM-5 catalyst at the same conditions. In 2002, they also studied NO_x reduction on the newly zeolite material, ITQ-7, which has a pore topology formed by a tridirectional system with 12-member ring similar to the structure of beta zeolite. They found that ITQ-7 when exchanged with copper or cobalt was an active catalyst for the SCR of NO with propane. And they also studied the effect in the presence of oxygen, water,

and sulphur dioxide, obtaining the best results at low oxygen concentration (1.5–2.5% O₂) and in the absence of water and SO₂.

Metal-exchanged zeolite catalysts have proven to be a less costly and more effective option for NO_x removal from flue gases. Although many zeolites have been used to decompose N₂O at higher temperatures, cobalt- or copper- ZSM-5, mordenite, and beta zeolites are emerging as the preferred choices due to their selectivity, availability, and relative cost (Adelman *et al.*, 2002).

2.5 Zeolite

Zeolites are crystalline, aluminosilicates materials with uniform pore size distribution that in nanometer with high internal surface area. The structure of zeolites depends on type of zeolite, their cations, and on type of chemical treatments.

The structure of a conventional zeolite consists of a three-dimensional framework structure of channels and cavities formed by SiO₄ and AlO₄ tetrahedral, which are termed T-atoms or tetrahedral atoms, where T is silicon or aluminum. T-atoms are bonded by the oxygen atoms, which are called the oxygen bridge at the corners of the tetrahedral. Those T-atoms arranged in a several ways giving the results as difference structures.

The ratio between Si and Al atoms in a zeolite can be varied. The trivalence of aluminium causes a net negative charge of the framework. This is compensated for by cations occupying certain extra-framework positions. The presence of aluminium in the structure can be represented to the acidity of zeolite. During synthesis, the cation is generally sodium or ammonium, but it can be exchanged with other cations. The results are many opportunities for new catalyst formulations. The type of cation can affect to the ion-exchange, adsorptive, and catalytic properties of zeolite.

Based on the powerful structure, stability, and activity of zeolites have led them to a variety of applications as molecular sieves, catalysts, adsorbents and ion exchangers with high capacities and selectivities. Thus, zeolites play an important role for the fuel, petrochemical industries, in the efficient use of raw materials, in energy efficiency, and in pollution control. In addition, zeolites can be modified by

ion-exchanging with active materials such as catalytic metals to enhance their catalytic activities.

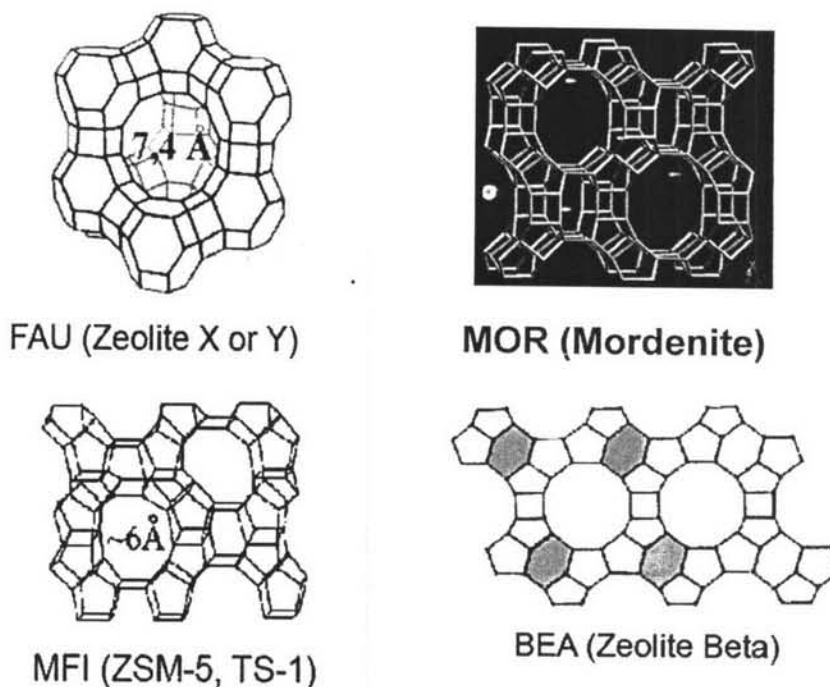


Figure 2.2 Some types of well-known zeolites (<http://topaz.ethz.ch>: accessed on 08/04/2005).

The first generation of zeolites (e.g., A, X, Y, and mordenite) generally has a high ion-exchange capacity as the low silica-to-alumina ratio. They have a high affinity for water that makes them widely used as desiccants and also other polar molecules adsorber. The second generation of zeolites (e.g., ZSM-5 and silicalite), which alkali cations are used during synthesis has higher silica-to-alumina ratio. These highly silica materials are effective for adsorbing organic molecules, even in low-concentration, high-humidity, and high temperature applications. A third generation of zeolites is the aluminosilico-metal phosphates (AlPO_4 , SAPO, MeAlPO, etc.) synthesized without alkali cations present, but using organic amines and ammonium compounds as structure-directing agents (Marcus and Cormier, 1999).

Recently, some of research groups have succeeded in creating new zeolite structures such as ITQ-series using organic molecules as structure-directing agents to yield a desired pore size or shape. The result is an increasing of some catalytic potentials related to the conventional zeolites.

2.6 ITQ-21

ITQ-21 (Instituto de Tecnología Química number 21), the silicogermanate material, is a new zeolite with large pore sizes and adequate Si/Al ratios. Generally, ITQ-21 in its calcined form has the chemical composition as $X_2O_3 : nYO_2 : mZO_2$ wherein $(n+m)$ is at least 5, X is a trivalent element, Z is Ge, Y is at least one tetravalent element other than Ge, and the ratio is $m/(n+m)$ is 0.0 to 0.5 (Diaz-Cabanas *et al.*, 2005). The channel system of ITQ-21 is three-dimensional channels of 0.74 nm diameter, with 6 circular opening windows comprising 12-membered rings. The three linear channels intersect perpendicularly to produce large inner cavities of 1.18 nm diameter. In this structure, the molecules formed inside that cavity can readily diffuse out through the six windows that are opened to the exterior. The synthesis of this material has been achieved through an ingenious combination of the structure directing effect of large organic molecules and framework atoms (germanium) (Corma *et al.*, 2002).

Figure 2.3 shows the outer T atoms of the clusters, that is, cage $[4^66^{12}]$ interconnected via double four-membered rings (D4MR). Each tetrahedral intersection represents one T site (either occupied by Si or Ge) bridged by O atoms. Inside the small box of Figure 2.3, the detailed structure of the complete cluster illustrates the four-membered ring. This ring is assumed to be randomly oriented normal to the three cell axes.

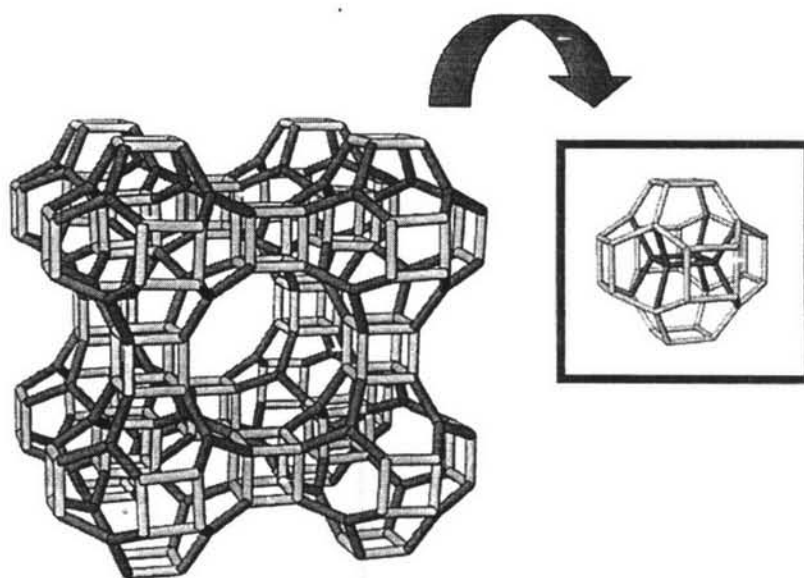


Figure 2.3 Perspective view of the unit cell of ITQ-21 (Corma *et al.*, 2002).

The structure is stable when heated at temperatures higher than 700°C, even in the presence of steam, and is able to support acid sites in the framework. The presence of the acid sites and the widely open structure of this zeolite allow it to produce a high quality gasoline, while giving high yields of propylene. These yields were only achieved by combining the effect of two zeolites: Y and ZSM-5.

New catalytic applications are found for this material in the field of aromatic alkylation, and hydrocracking, as well as for the incorporation of organic dyes as guest species for producing zeolite-dye micro-laser and light emitting devices.

ITQ-21 can be synthesized from different methods. In the presence of fluoride, the ions act as mobilizing agents of silica with using N(16)-methylsparteinium as the structure directing agent that gives rise to organic cations stable in the reaction medium (Diaz-Cabanas *et al.*, 2005). And, in the absence of fluoride ions method spent longer crystallization time (Corma *et al.*, 2005).

Blasco *et al.* (2004) studied on the synthesis of ITQ-21 catalyst. They reported that, at Si/Ge = 5, 100% crystallinity of catalyst was obtained after only 6 hours. And, they can obtain the crystalline size of catalyst in the range of 80 nm to 2 μm by controlling the H₂O/Tetrahedral atoms ratio. In addition, they confirmed that

ITQ-21 possessed high thermal and hydrothermal stability when Si/Ge ratio was above 10.

Many experiments have been proposed in order to study the roles of germanium in ITQ-21. Bu and Feng (2003) found that Ge helped to stabilize the D4R, and it can reduce the crystallization time during catalyst synthesis. Zwijnenburg *et al.* (2004) and Li *et al.* (2004) found that by increasing Ge/(Ge+Si) ratio, the metastability of D4R increased. Blasco *et al.* (2004) found that by increasing Ge loading, the crystal size of the catalyst increased, but the external and BET surface area decreased. And Salguero *et al.* (1997) suggested that with the addition of germanium, both of the acidity and the number of strong acid sites of catalyst decreased.

Arribas *et al.* (2004) found that ITQ-21 had relatively high surface area and pore volume when compared with Y and Beta zeolites. And, they also found that ITQ-21 contained the highest number of total acidity required in NO_x reduction, when compared with those zeolites as shown in Table 2.3.

Table 2.3 Relative acidity of zeolites as determined by pyridine adsorption-desorption experiment (Arribas *et al.*, 2004)

Catalyst	Bronsted			Lewis		
	250°C	350°C	400°C	250°C	350°C	400°C
ITQ-21	100	42	17	180	145	145
USY	95	53	20	57	30	22
Beta	87	68	53	95	65	62