Basicity of MgO by Temperature Programmed Desorption of Phenol

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Abstract

Temperature programmed desorption (TPD) of phenol on MgO was studied using several detection techniques including thermal conductivity, infrared spectroscopy, differential thermo-gravimetric analysis and differential scanning calorimetry to explore the surface sites of the catalysts. It was found that phenol is an effective probe molecule for both qualitative and quantitative in the determination of the surface sites on MgO. The different surface sites of different basic strength can be distinguished via the desorption profiles obtained as phenol is desorbed with the increasing temperatures. Results from all techniques are in agreement. Three chemisorption peaks are observed. They could be attributed to the flat surface sites exposure {100} and surface sites of low coordination number, edges and corners. The amount of coverage on each site was also determined.

Key words : Basicity of MgO; Base strength distribution; Active sites on MgO; Temperature programmed desorption of phenol; Detection techiniques for probe molecule

Introduction

Magnesium oxide is recognized and widely used as a solid base catalyst and support for a variety of reactions(1-6). Catalytic interest lies largely in its basic surface character. As a result of extensive electron transfer from magnesium to oxygen upon MgO formation, the electron rich-oxygen anions on MgO surfaces act as strong basic, electron-donating sites, while the electron deficient magnesium cations act as weak acid, electron-accepting sites(4). A number of catalytic reactions over MgO, including isomerization of alkenes, alkynes, and unsaturated compounds containing heteroatoms, amination and hydrogenation of alkenes and conjugated dienes, hydrogenation of CO, and decomposition of alcohols, amines, and esters(7) all involve heterolytic dissociation of molecules via an acid-base interaction on the catalyst surface.

An intriguing aspect of the basic properties of MgO arises from the surface inhomogeneity of this material(4). Three types of surface sites on MgO have been proposed and assigned to surface MgO pairs with different coordination numbers, 5-fold-coordinated sites (on the extended MgO(100) plane), 4-fold-coordinated sites (on the edges between the (100) plane), and 3-fold –coordinated sites (on kinks and corners). Sites of lower coordination have been reported to exhibit stronger basicity, and are thus capable of reacting with weaker acids.

The basic strength of a solid surface is defined as the ability of the surface to donate an electron pair to an adsorbed acidic gas. Basicity is expressed as the number (or mmol) of basic sites on the solid surface per unit weight or per unit surface area of the solid(8). There are two main methods used to explore basic strength and basicity; benzoic acid titration using indicators, and the adsorption of gaseous acids. The benzoic titration method is generally not suitable for measuring the basicity of a catalyst because it is carried out at room temperature which is significantly different from the usual operating conditions of catalytic reactions (9). Adsorption of acidic gases is therefore preferred and the most widely used for the measurement of basicity. Probe molecules which have been used include carbon monoxide(10), carbondioxide(9,11), sulphur dioxide(12), hydrogen(13), phenol(14), water(15), pyrole(16),

chloroform(17), acetonitrile(18), alcohols(19), thiols(20), boric acid trimethyl ether(21), ammonia(22) and pyridine(23). However, it was concluded that no probe can be universally used(24).

Further research to search for proper probe molecules as well as techniques that can clarify both adsorbed species and the amount of species formed was warranted. As a consequence the aim of our work is to investigate the chemical behaviour of both probe molecule and the surface of MgO as well as identify the effective method to determine its surface sites and their relative basicity.

Experimental

Temperature programmed desorption of phenol on MgO calcined from $Mg(OH)_2$ at different temperatures,400˚C, 600˚C and 800˚C were investigated. Different approaches were attempted. $Mg(OH)_2$ was prepare by precipitation of 2M $Mg(NO_3)_2$ solution ($Mg(NO_3)_2.6H_2O$(BDH, AR grade) with ammonia solution (BDH, AR grade) at pH 10.0. The precipitate was washed with deionized water and dried in a vacuum oven at 120˚C for 3 hour. This $Mg(OH)_2$ was ground and sieved (180 mm sieve) before calcination.

TPD of phenol from MgO with thermal conductivity detector (TCD)

Approximately 10 mg of $Mg(OH)_2$ was packed between quartz wool in a quartz tube 27 cm long and 0.7 cm in diameter. The sample was then calcined under helium (high purity, CIG) atmosphere at a flow rate of 30 mL/min. The calcined MgO sample was cooled to room temperature under helium and then exposed to phenol by switching the carrier gas to pass, in series, through the phenol (Aldrich 99+ dried with $CaSO_4$) and the sample. The sample was exposed to phenol for half an hour. Excess phenol was removed by flowing helium until a constant base line on the recorder was obtained. Temperature programmed desorption was then carried out with a heating rate of 5˚C/min to 800˚C and a carrier gas flow rate was 30 mL/min. The TPD profile was acquired by means of a thermal conductivity detector (TCD) which was interfaced to both a chart recorder and computer. The flow-chart of the TPD apparatus is shown in Figure 1.

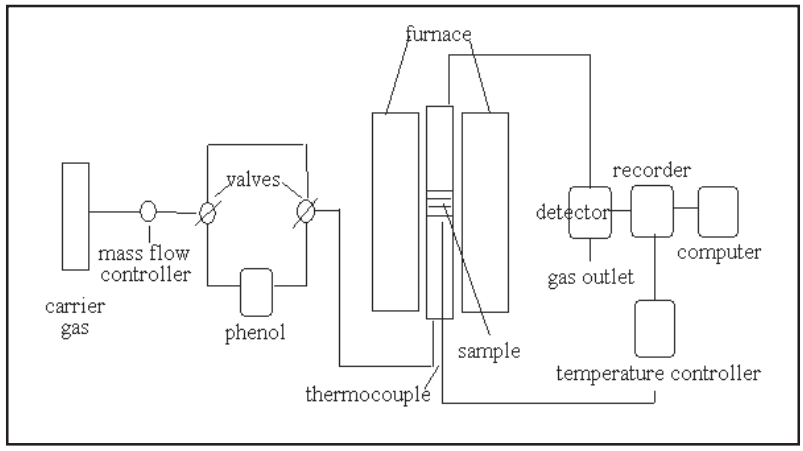


Fig. 1 TPD apparatus with thermal conductivity detector(TCD).

TPD of phenol from MgO with thermo-gravimetric (TG) detector.

A Setaram TGA 92 thermoanalyser which consists of a vertical furnace (capable of being heated to 1800°C), a thermobalance (± 0.01 mg) and a CS 92 controller for controlling programmable heating rates from 0.1 to 99.9°C/min, was used to investigate the weight loss from samples of MgO which had been exposed to phenol.

Approximately 100 mg of MgO precursor was calcined at desired temperatures under argon, cooled to room temperature and exposed to phenol as described in sections 2. The MgO was divided into two portions. One was transferred to a pretared alumina crucible and placed in the TGA92. The other portion of MgO was transfer to the a DSC aluminium crucible (6 mm inner diameter and 5 mm long).

TPD of phenol using Differential Scanning Calorimetry (DSC)

A Setaram DSC 92 differential scanning calorimeter (composed of CS 92 controller, DSC 92 calorimeter, PC 92 computer and a printer) was employed to analyse the enthalpy change of the desorption of phenol from the surface of MgO.

Infrared spectra of phenol adsorbed on MgO

Approximately 15-20 mg of $Mg(OH)_2$ was compressed into a self- supporting disc of 11 mm in diameter and mounted in the cell. It was then calcined under argon (CIG, high purity) at a flow rate of 10 mL/min at desired temperatures (400,600 and 750˚C for 4 h) and cooled to room temperature. A background infrared spectrum of MgO was recorded by a Digilab FTS-20E FTIR Spectrophotometer over the frequency range 4000 cm^{-1} to 1000 cm^{-1}. The sample was then exposed to the phenol (Aldrich 99 % +) for 30 min (at a carrier gas (argon) flow rate of 10 mL/min) and then purged with carrier gas for 1 h at a high flow rate of 50 mL/min. The MgO was then heated at a rate of 5˚C/min and the spectra were recorded at a range of temperatures. The background MgO spectrum was subtracted from each of the obtained spectra.

Results

TPD of Phenol on MgO using TPD detector.

TPD profiles of phenol on MgO samples calcined from $Mg(OH)_2$ at different temperatures by TCD detector are displayed in Figure 2.

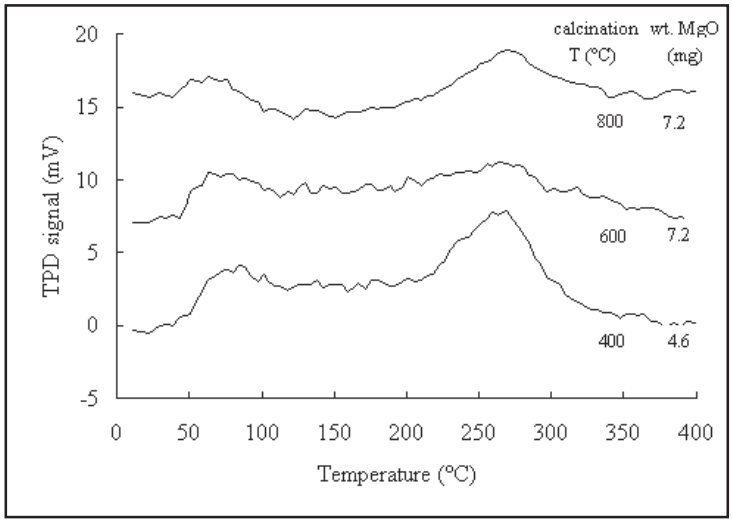


Fig. 2 TPD profiles of phenol on MgO samples using TCD detector.

Two distinct peaks at 75˚C (348 K) and 275˚C (548 K) were observed for the temperature programmed desorption (linear ramp rate 5˚C/min) of phenol from MgO. These two peaks may be attributed to the physisorption and chemisorption of phenol on MgO; the TPD peak at being 75˚C attributed to physisorption and the peak at 275˚C representing chemisorption. It is likely that there may be an additional chemisorption peak at ca. 160-180˚C. To clarify this a new approach was employed as described in the next section.

TPD of phenol on MgO by TG analysis.

From Figure 3 the differential weight loss (DTG) was plotted against the progressive temperature. The temperatures at which the maximum desorption (T_M) of phenol occurred were evaluated from the minimum positions of the DTG curve. From the DTG curves at the highest ramp rate three peaks are discernible at 75, 205 and 318˚C. At the lower ramp rate two peaks at 75 and 280˚C are clearly seen but the intermediate peak is not resolvable.

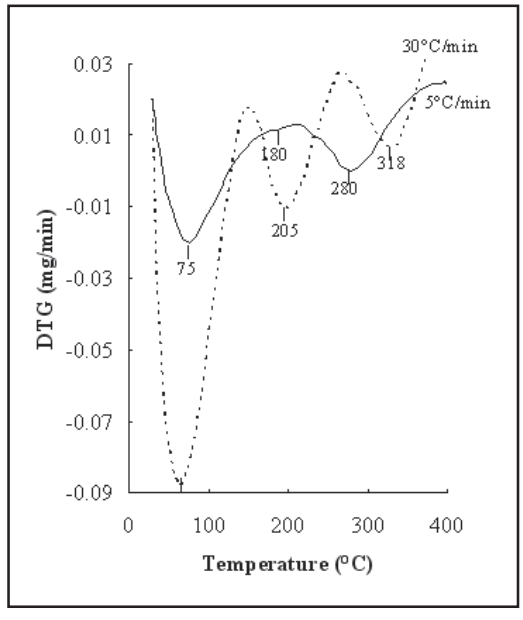


Fig. 3 TPD profiles of phenol on MgO (calcined from Mg(OH)2 at 600˚C) by the TG method with a ramp rate of 5˚C/min and 30˚C/min.

TPD of phenol by DSC method.

In Figure 4 it is noted that the TPD profiles obtained from DSC experiment are similar to that obtained from the TG experiment. Three desorption peaks were observed at 80, 180 and 280˚C for MgO calcined at 600˚C, and at 80, 180 and 308˚C for MgO calcined at 850˚C. These results strongly support the data obtained from the TG experiment.

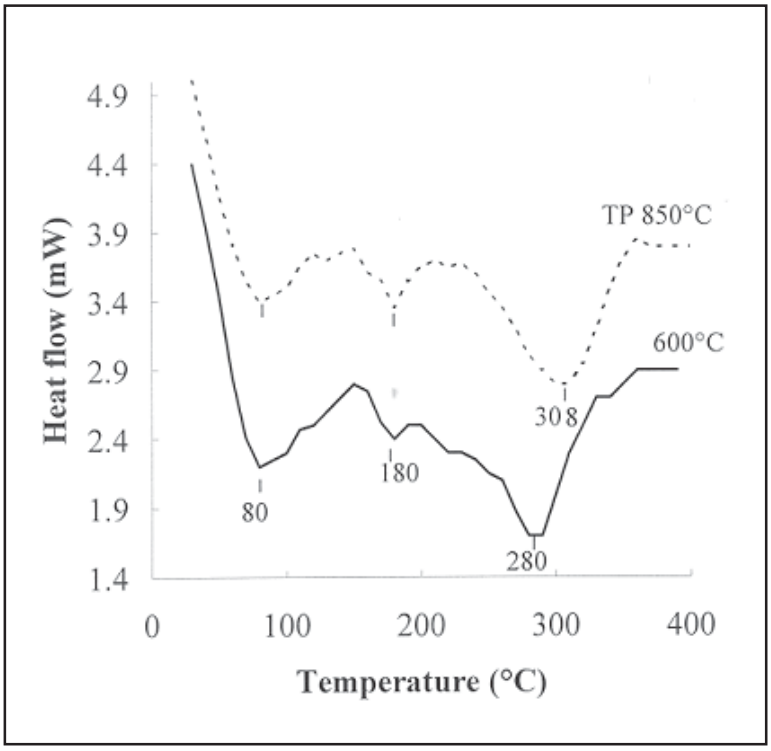
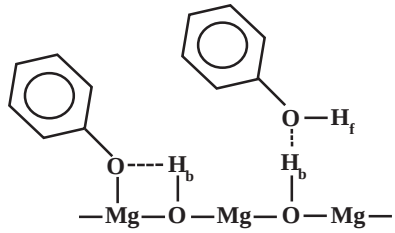


Fig. 4 TPD profiles of phenol desorbed from MgO calcined at 600 and 850˚C.

TPD of phenol by infrared spectroscopy.

From Figures 5 and 6 it can be observed that phenol adsorbed on MgO displays two strong absorption regions, namely at 2800-3650 cm^{-1} and 1300-1600 cm^{-1}. The broad band at 2800-3650 cm^{-1} significantly decreased with increasing temperature and disappeared at temperatures above 150˚C. This band is assigned to the absorption of OH species arising from the dissociative adsorption of proton from phenol adsorbed on the O^{2-} of the MgO surface (and a phenolate ion adsorbed on Mg^{2+}). At low temperatures these OH species may from a hydrogen bond with their near neighbours or physisorbed phenol that is loosely bound to this chemisorbed species as follows:



OHb = hydrogen bonded OH, OHf = free OH.

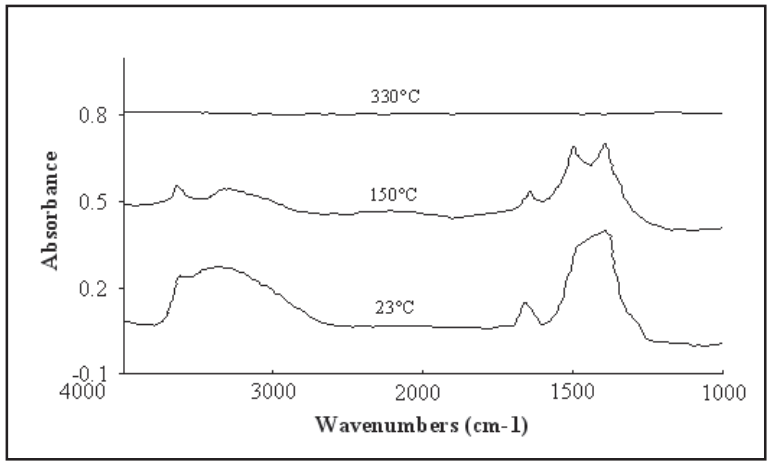


Fig. 5 TPD of phenol on MgO (calcined at 600 ˚C for 4 h).

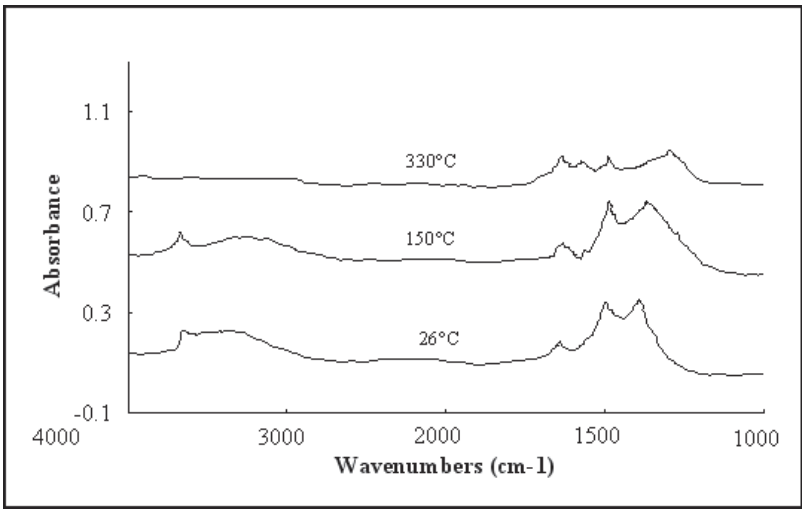


Fig. 6 TPD of phenol on MgO (calcined at 750˚C for 4 h).

As the temperature was increased to 150˚C this band become less prominent due to the elimination of the physisorbed species.

The absorption in the 1300-1600 cm^{-1} region was attributed to phenolate species, from the C=C stretching of the benzene ring of phenol and the C–O stretching vibration (14,25). The skeletal vibrations, involving C=C stretching within the ring, absorb in the 1600-1585 cm^{-1} and in the 1500-1400 cm^{-1} regions. The C–O stretching vibrations of phenols produce a strong band in the 1300-1000 cm^{-1} region. At room temperature and at 150˚C the absorption bands at 1650 cm^{-1}, 1600 cm^{-1} and 1300 cm^{-1} were observed only in low intensities, while two broad bands centred around 1500 cm^{-1} and 1380 cm^{-1} were clearly displayed.

It is likely that the broad bands centred at 1500 cm^{-1} and 1380 cm^{-1} were predominantly due to the absorption of phenolate species and undissociated phenol molecules that physisorbed on the chemisorbed species. The interaction amongst these species results in the broad absorption bands as observed at room temperature. As the temperature was increased, the physisorbed molecules were eliminated, and accordingly the physical interaction was reduced. The characteristic of these broad bands were still

observed at 150 ˚C, but with less intensity than that observed at the ambient temperature. This was postulated to be due to the interaction between the chemisorbed species and their neighbours which disappeared at higher temperatures (330 ˚C). At such a temperature all phenolate species were removed from the surface of MgO calcined at 600 ˚C. However, some evidence for free phenolate was observed for MgO calcined at 750 ˚C.

The bands at 1650 cm^{-1}, 1600 cm^{-1} and 1300 cm^{-1} indicate that the interaction among adsorbed molecules was eliminated due to the distance between these species. At 330 ˚C for MgO calcined at 750 ˚C, the intensity of absorption bands at 1650 cm^{-1}, 1600 cm^{-1} and 1300 cm^{-1} increased, while the broad band at 1500 cm^{-1} was found to decrease and the band centred at 1380 cm^{-1} almost disappeared. There was no sign of the adsorbed gas remaining on the MgO surface at 330 ˚C for the MgO sample calcined at 600 ˚C.

Discussion and Conclusion

According to the TPD results using DTG analysis and DSC data it can be concluded that there are three chemisorption peaks, T_M at about 180, 280 and 308˚C respectively. The desorption peak, T_M at ~ 180˚C indicates a site with a lower basic strength than the others observed at higher T_M. The second site is associated with the desorption peak T_M at 280˚C which was found at high intensity for the desorption of phenol on MgO calcined at 400˚C and 600˚C for 4 h. However, this peak was very weak or disappeared for the TPD of phenol on MgO calcined at 800˚C for 4 h, or 850˚C. The third site on the surface of MgO is indicated by the desorption with T_M at ~ 308˚C which was dominant for the desorption of phenol from MgO obtained at a high calcination temperatures.

Coluccia and Tench (26) have proposed a surface model of MgO calcined at different temperatures as shown in Figure 7.

It is likely that site S_I corresponds to the T_M at 280˚C. It is observed dominantly for MgO calcined at 400˚C and 600˚C for 4 h respectively. As the calcination temperature was increased to 800˚C this TPD peak disappears. On the other hand site S_{III} becomes dominant at high pretreatment temperature of 800˚C and over. This site is therefore attributed to the desorption with T_M at 308˚C which

was observed only for MgO calcined at temperatures ≥ 800˚C. Site S_{II} is therefore assumed to be represented by the desorption with T_M at 180˚C.

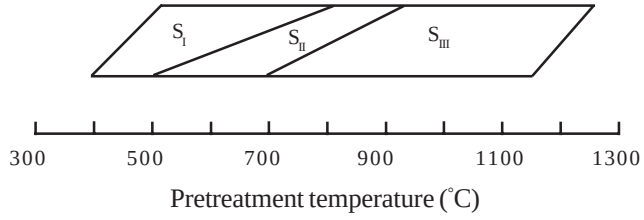


Fig. 7 Three types of sites on MgO with increasing pretreatment temperature (26).

All these sites, S_I, S_{II} and S_{III}, have been assigned to the low coordinated (lc) ions, O_{lc}^{2-} and Mg_{lc}^{2+}, on MgO surfaces (7). From the T_M's which indicate the basic strength of each site and from the work of Hattori (7) and Dunski et al. (15), the desorption with T_M at 305˚C, site S_{III}, which displays the highest basic strength should consist of the high ratio of the lower coordination site, the corners, i.e. $Mg_{3c}^{2+}O_{3c}^{2-}$, $Mg_{4c}^{2+}O_{3c}^{2-}$, $Mg_{3c}^{2+}O_{4c}^{2-}$. According to Hattori (7) and Dunski et al. (15) these unsaturated sites were mostly generated when high pretreatment temperatures (>800˚C) were used. The TPD of phenol from MgO with T_M at 280˚C, site S_I, shows a lower basic strength than that of the desorption with T_M at 308˚C but higher than that of the desorption with T_M 180˚C, site S_{II}. From earlier work (15) it should therefore be composed of higher coordination number of O_{lc}^{2-} and Mg_{lc}^{2+} ions than those of the corners, but lower than those of the site represented by the desorption with T_M at 180°C. Extended edges are possibly the major contributor for site S_I. At higher calcination temperatures the lower coordinated ions, the corners, are generated. The combination of the edges and the corners create a new site represented by the desorption with T_M at 308°C, site S_{III}. Due to its lowest basic strength, the desorption with T_M at 180°C, site S_{II}, should represent the $Mg_{5c}^{2+}O_{5c}^{2-}$ on the flat surface of MgO (Figure 8).

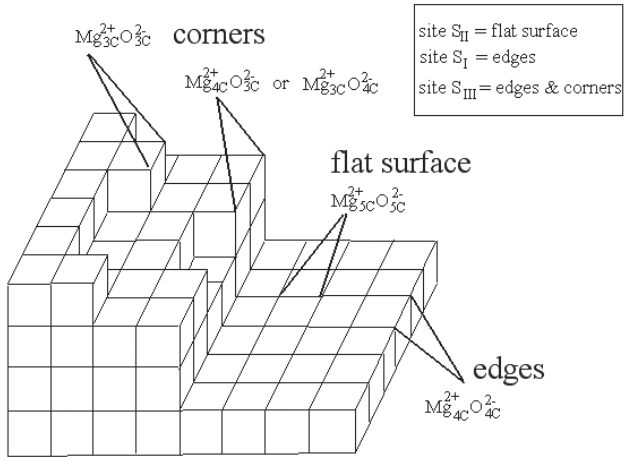


Fig. 8 Model for the low coordination sites on MgO surface.

The amount of phenol adsorbed on the chemisorption sites S_I, S_{II} and S_{III} was determined from the weight loss of the adsorbed sample under the progressive temperature change. It was found that different calcination temperatures results in different basicities for each site as shown in the Table 1.

Table 1 The basicities (mmol of phenol/weight of MgO) of MgO obtained from $Mg(OH)_2$ precipitated at pH 10.0 and calcined at different temperatures.

calcination (°C)	site S_I (mmol/g)	site S_{II} (mmol/g)	site S_{III} (mmol/g)	ratio of sites site S_I	site S_{II}	site S_{III}
400	0.34±0.04	0.15±0.03	-	7	3	-
600	0.30±0.03	0.17±0.03	-	5	3	-
800	-	0.11±0.03	0.15±0.03	-	2	3
850	-	0.14±0.03	0.15±0.03	-	1	1

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