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Balancing acidity and basicity for highly selective and stable modified MgO catalysts in the alkylation of phenol with methanol

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Abstract

The alkylation of phenol was investigated over magnesium oxide catalysts modified with the addition of small amount of vanadium, manganese or other components. The catalytic performance was strongly dependent on the kinds of dopants due to changes in the acid–base properties. The modified MgO catalysts showed an activity higher than pure MgO catalyst. V–Mn–MgO catalyst was found to be more active and selective than that of V–Mgo or Mn–MgO catalyst for 2,6-xylenol. Among the modified catalysts, V–Mn–MgO catalyst was excellent in both phenol conversion and the selectivity to 2,6-xylenol. The alkylation of phenol in *ortho* position was explained in the acid–base property of mixed oxide. Phenol conversion and 2,6-xylenol selectivity increased with acidity, whereas the selectivity to *o*-cresol decreased because of the nature of the series reaction (phenol → *o*-cresol → 2,6-xylenol → 2,4,6-trimethyl phenol (2,4,6-TMP)). Na–Mn–MgO catalyst prepared to achieve a balance between acidity and basicity was not deactivated and highly selective to *o*-cresol and 2,6-xylenol. Reaction temperature, feed composition and space velocity also significantly influenced the conversion and the selectivity in the alkylation of phenol. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Alkylation; Phenol; 2,6-Xylenol; Modified magnesium oxides

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1. Introduction

Alkyl phenols prepared by the alkylation of phenol (PhOH) with methanol (MeOH) are industrially important intermediates in the agrochemical, pharmaceutical and polymer industries. For example, *o*-cresol is used in the synthesis of herbicides and 2,6-xylenol is a monomer in the manufacture of polyphenylene oxide (PPO) and special-grade paints [1].

The alkylation of phenol is a thermodynamically feasible reaction, however, few catalysts are commercialized and the proposed catalysts are suffered from the rapid deactivation and the low activity. A large number of related patents and papers have appeared on the synthesis of alkyl phenols over various catalysts [2–15]. Only a few studies have reported the catalytic activity and selectivity and the mechanism on the alkylation of phenol [16–21]. These studies revealed that there was always a competition between O- and C-alkylation and the strength of acid sites played an important role on the product selectivity.

Woo et al. [22,23] reported the aniline alkylation with methanol over boronsilicates catalysts, and correlated their studies of temperature programmed desorption (TPD) on these catalysts with the catalytic

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activity and acidity. Marczwski et al. [24] studied the alkylation of phenol with methanol in the presence of ultrastable HY zeolite. The product distribution showed that anisol, *ortho*- and *para*-cresol were the main products of the reaction. O-alkylation was about three times as fast as C-alkylation. Tanabe and co-worker [16,18] reported that the catalysts having higher acidic strength were more active but less selective to *ortho*-alkylation. The basic oxide such as TiO_2–MgO was highly selective towards 2,6-xylenol, whereas the acidic catalysts such as SiO_2–Al_2O_3 were not highly selective. Hamilton [25] found that MgO catalyst was highly selective to C-alkylation in the phenol alkylation.

Magnesium oxide catalyst is known to be favorable in the synthesis of *o*-cresol and 2,6-xylenol but has a low activity. In order to improve their catalytic performance, several kinds of components were doped to MgO. On increasing the acidity of the catalyst, by addition of acidic components, the catalytic activity increased. However, the selectivity towards *ortho*-alkylated products decreased. The *ortho*-selectivity was attributed to a combination of weakly acidic sites and strong basic sites present on the catalyst surface [19].

This research was intended to develop excellent magnesium oxide catalysts modified with the addition of small amount of vanadium, manganese, or other components. And the catalytic performance and the deactivation properties of these modified catalysts were evaluated.

2. Experimental

2.1. Catalysts

Modified magnesium oxide catalysts were prepared by mixing the solution of dispersed basic magnesium carbonate and the solution of doped metal compounds [26,27]. This mixed solution was evaporated in rotary evaporator and dried at 120°C for 24 h. These pre-dried materials were crushed and sieved to 100–200 mesh size particles. These catalysts were calcined at 500°C for 2 h in oxygen stream. The surface areas of prepared catalysts were measured by the BET method using nitrogen adsorption at 77 K.

2.2. Apparatus and procedure

The phenol alkylation with methanol was carried out at atmospheric pressure using a differential tubular reactor system. Reactor was a 0.95 cm diameter stainless steel tube. 0.1 g of catalyst was placed on quartz wool in the tubular reactor. The reactant feed rate (phenol-to-methanol molar ratio = 1:5) was controlled by a liquid syringe pump (Sage Instrument, Model 355) and introduced to pre-heating zone (250°C) to perform the gas phase reaction. These gas phase reactants were carried to the catalysts by N_2 carrier gas. Reaction products were collected in ice-trap and analyzed using gas chromatography (Varian Aerograph, Series 1400) with a packed column of 25% silicon DC-550 on chromosorb W. The conversion of phenol is defined as the percentage of the moles of consumed phenol to the moles of phenol in feed. The selectivity to specific product is defined as the moles of specific product divided by the moles of consumed phenol.

3. Results and discussion

3.1. Performance of various modified MgO catalysts

The alkylation of phenol with methanol was carried out using magnesium oxide catalyst alone or in addition of other dopants. Tables 1 and 2 summarize the conversion and the selectivities of the prepared catalysts. The modified MgO catalysts are found to be more active and selective than pure MgO to 2,6-xylenol. Among the modified MgO catalysts, copper doped and vanadium doped MgO catalysts showed the good selectivity to 2,6-xylenol and the high activity. It might be thought that the acid–base properties of the catalysts could be modified by the addition of dopants.

Fig. 1 shows the catalytic performance on various modified MgO catalysts with reaction time. The activity of pure magnesium oxide was low and gave only *o*-cresol as an alkylation product. A small amount of addition of dopants into the magnesium oxide gave better activity and the selectivity to 2,6-xylenol than the pure MgO catalyst as shown in Fig. 1. V–MgO catalyst has the good activity and the selectivity to 2,6-xylenol as compared with other catalysts. The

Table 1
Alkylation of phenol over single component doped magnesium oxide catalysts[a]

Catalysts[b]	PhOH conversion (%)	Selectivity (%)			
		o-Cresol	2,6-Xylenol	2,4,6-TMP	By-products
MgO	8.2	100	–	–	–
Mn(2.5)–MgO	40.6	83	17	–	–
Ga(2.5)–MgO	44.4	63.1	36.9	–	–
V(1)–MgO	58.4	73.7	26.3	–	–
V(2.5)–MgO	64.5	53.5	39.1	4	2.4
V(5)–MgO	62.5	60.2	32.5	3.8	3.5
Ni(3.5)–MgO	52.8	78.9	21.1	–	–
Co(1)–MgO	42.1	80.9	19.1	–	–
Cr(2.5)–MgO	49.2	75.7	19.8	1.4	3.1
Cu(3.5)–MgO	59.9	58.8	33.9	7.3	–

[a] All values were the average at about 1 h after the start of the reaction. Reaction conditions: temperature = 460°C; reactant flow rate = 0.27 cc/h; PhOH/MeOH mole ratio = 1/5; flow rate of N_2 carrier gas = 10 cc/min; catalyst = 0.1 g.

[b] The value in the parenthesis refers to mol%.

conversion and selectivity were significantly varied with the reaction time. V–MgO catalyst deactivated rapidly during the reaction period while Mn–MgO catalyst did slowly.

In order to examine the effect of amount of vanadium on MgO, the phenol conversion and the selectivities to *o*-cresol and 2,6-xylenol were obtained as shown in Fig. 2. At the beginning of reaction the phenol conversion on V(2.5 mol%)–MgO was 64.5% and the selectivity to 2,6-xylenol was 39.1%. A further increase of vanadium from 2.5 to 5% gave the less activity and the selectivity to 2,6-xylenol. However, an increase of vanadium content resulted in an increase in 2,4- and 2,5-xylenols selectivities as shown in Table 1. Since the acid strength of higher loading of vanadium is higher, the acid sites interact with the π-electrons of the benzene ring of phenolate, giving more side products [16]. During the reaction period, the catalysts with higher loading of vanadium deactivated more rapidly than that with less loading of vanadium. It can be explained by the fact that the large amount of vanadium on magnesium oxide is more acidic and the strong acidic sites seem to be easily deactivated, probably by carbonaceous deposits [17]. It indicates that an appropriate acid–base bifunctional property is required for high conversion and selectivity to 2,6-xylenol.

In an effort to improve the activity and the selectivity of the catalyst, the modified magnesium oxide catalysts containing more than one component were prepared and examined as listed in Table 2. Two component doped MgO catalysts are more active and selective to 2,6-xylenol than single component doped MgO

Table 2
Alkylation of phenol over two component doped magnesium oxide catalysts[a]

Catalysts[b]	PhOH conversion (%)	Selectivity (%)			
		o-Cresol	2,6-Xylenol	2,4,6-TMP	By-products
V(1)–Mn(1)–MgO	76	57	39.6	2.4	1
V(2.5)–Mn(1)–MgO	91.7	30.1	47.6	16.7	5.6
Ga(2.5)–V(1)–MgO	37.2	81.8	18.2	–	–
Na(1)–Mn(1)–MgO[c]	30	88.1	7.6	4.3	–
Sb(1)–V(1)–MgO[c]	83.7	32.7	56	9.2	2.1

[a] All values were the average at about 1 h after the start of the reaction. Reaction conditions are the same as in Table 1.

[b] The value in the parenthesis refers to mol%.

[c] Amount of catalyst = 0.2 g and flow rate of N_2 carrier gas = 6 cc/min.

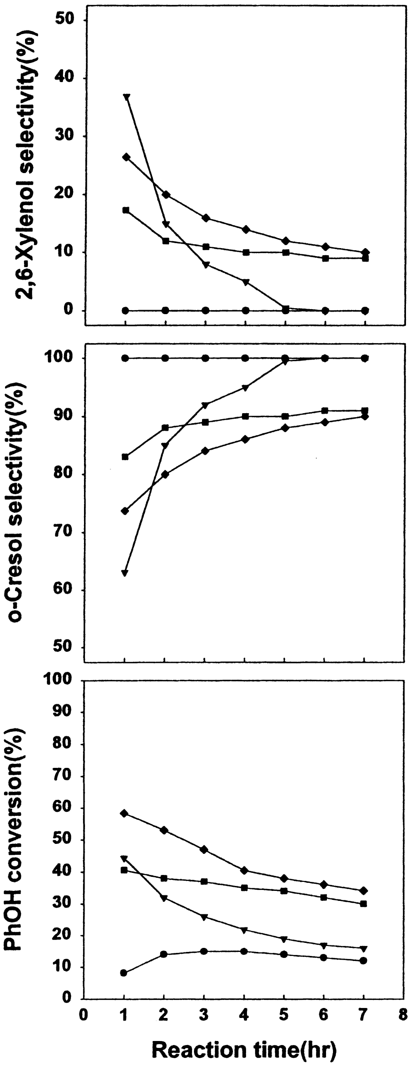

Fig. 1. Catalytic performance of various modified MgO catalysts. MgO (●), Ga(2.5%)–MgO (▼), Mn(2.5%)–MgO (■) and V(1%)–MgO (◆). Reaction conditions: temperature = 460°C; feed rate = 0.27 cc/h; flow rate of N_2 carrier gas = 10 cc/min; catalyst = 0.1 g.

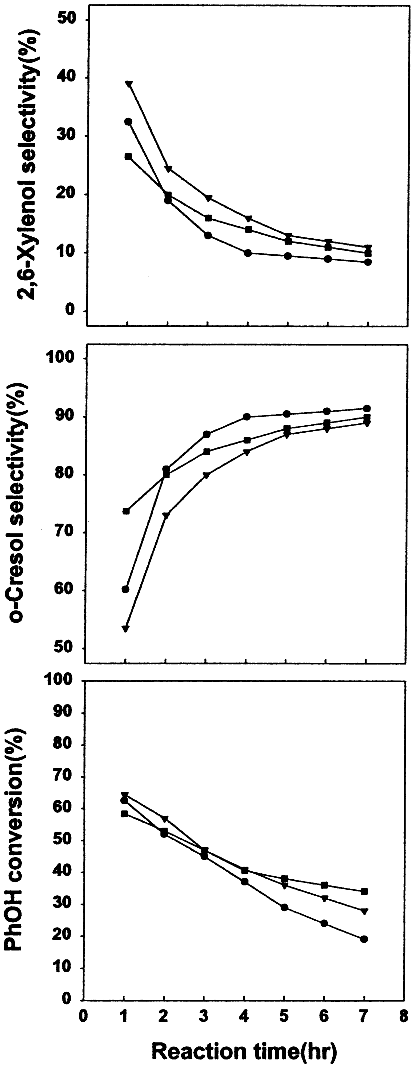

Fig. 2. Effect of vanadium content on phenol conversion and product selectivities. V(5%)–MgO (●); V(2.5%)–MgO (▼); V(1%)–MgO (■). Reaction conditions are the same as Fig. 1.

catalysts. It indicates that changes in the acid–base properties take place on the catalysts for the alkylation of phenol with methanol. The catalytic performance of V–Mn–MgO catalyst is shown in Fig. 3 and it is compared with V–MgO and Mn–MgO catalysts. At the beginning of the reaction, the activity of V–Mn–MgO catalyst was significantly higher than that of V–MgO or Mn–MgO catalyst. The V–Mn–MgO catalyst was excellent in both the conversion of phenol and the selectivity to 2,6-xylenol. However, the conversion of phenol and the selectivity to 2,6-xylenol decreased sharply with reaction time while the selectivity to *o*-cresol increased. Such a decrease in conversion and a change in selectivity might be due to the deactivation of active sites. It is considered that the deactivation of active sites results from the deposition of carbonaceous materials onto the catalyst.

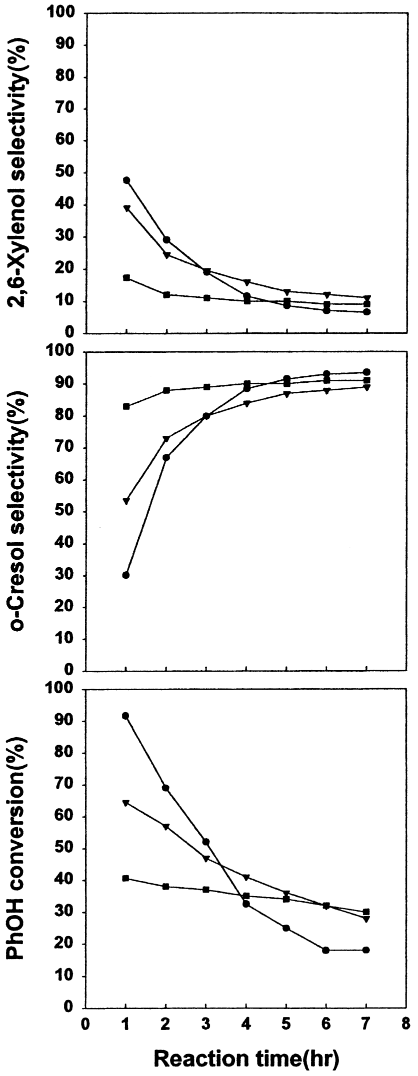

Fig. 3. Comparison of V–Mn–MgO catalyst with V–MgO and Mn–MgO catalysts. V(2.5%)–Mn(1%)–MgO (●); V(2.5%)–MgO (▼); Mn(2.5%)–MgO (■). Reaction conditions are the same as Fig. 1.

From our results, it is certain that V–Mn–MgO catalyst brings out a combined effect or sort of synergistic behavior enhancing the catalytic activity. Furthermore, it is believed that the acidic and basic character of the catalysts would affect the product selectivity. The catalysts with higher acidic strength are more active but less selective to *ortho*-alkylation. It seems reasonable that there is an interaction between the electrons which are distributed at benzene ring and the acidic sites on the surface of acidic catalyst. So it is easy to attack on *m*- and *p*-carbon of phenol by the adsorbed methyl group [24]. This agreed with our results in which the catalyst with more acidity produces more by-products such as 2,4- and 2,5-xylenols.

It is important to note that Na–Mn–MgO gives a good catalytic performance on the alkylation of phenol even though it has lower activity than V–Mn–MgO catalyst. Na–Mn–MgO catalyst showed that the activity and the selectivity to 2,6-xylenol were higher than those of pure MgO catalyst. Since the Na–Mn–MgO catalyst was prepared for good acid–base balance, the phenol conversion and the selectivities to *o*-cresol and 2,6-xylenol were maintained without the rapid change during the reaction, and the selectivity to *ortho*-alkylated products was very high. Also, the deactivation of catalyst was not observed during the alkylation of phenol. This can be explained in terms of the reaction mechanism of phenol alkylation proposed by Hamilton [25]. The basic sites are needed for methanol dehydrogenation, whereas the acidic sites are needed for methylation through methanol dehydration. Therefore, the active sites balanced with acidic and basic sites might be present onto the catalyst and HCHO should be coordinated to Mg cation of MgO. In this case, the basicity of Mg cation plays an important role in the alkylation of phenol. However, if the strong acidic site is present in the vicinity of Mg cation as Brönsted acid type, the balance of acid and base will be lost because of the influence of its acidic site into the basicity and then the catalytic activity and the selectivity will go down. Thus the balance of acid–base property is very important for phenol alkylation. From the above explanation there must be some catalytic stability including good balanced acid–base property by the addition of sodium.

3.2. O- and C-alkylation and influence of acidity

C-alkylation of phenol over MgO has been reported earlier [25] and the basic catalyst gave predominantly C-alkylation, whereas an increase in acidity decreased C-alkylation, selectively increasing O-alkylation [28]. Our results showed that 100% selectivity of *o*-cresol was obtained with pure MgO catalyst and small amounts of anisole with V–Mn–MgO catalyst. Anisole by means of O-alkylation can be formed through the

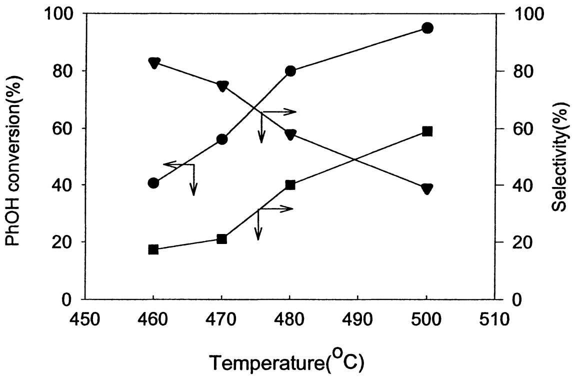

Fig. 4. Effect of temperature on phenol conversion and product selectivities of Mn(2.5%)–MgO. Conversion of phenol (●) and selectivities to *o*-cresol (▼) and 2,6-xylenol (■). Reaction conditions are the same as Fig. 1 except for reaction temperature.

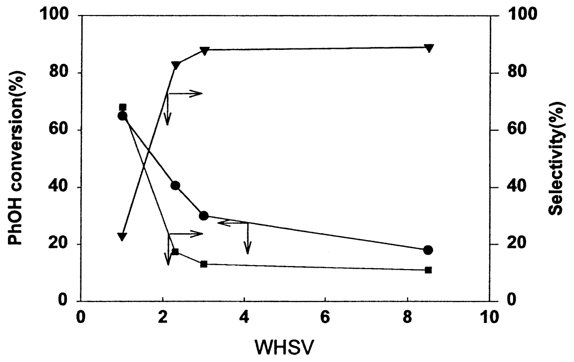

Fig. 5. Effect of space velocity on phenol conversion and product selectivities of Mn(2.5%)–MgO. Conversion of phenol (●) and selectivities to *o*-cresol (▼) and 2,6-xylenol (■). Reaction conditions are the same as Fig. 1 except for space velocity.

$\mathrm{S_N}2$ reaction between phenol and methanol which is adsorbed on Brönsted acidic sites [20], but the adsorbed anisole can be changed to *o*-cresol on acidic catalyst by isomerization [29]. Also, *o*-cresol is produced with methanol dehydration on acidic catalyst. Therefore, as we can see in Fig. 2, the high selectivities to the *o*-cresol and 2,6-xylenol could be obtained not only in basic MgO but also in acidic V–Mn–MgO.

3.3. *Effect of reaction conditions*

Studies on the effect of temperature on alkylation of phenol were carried out over Mn–MgO catalyst in the temperature range 460–500°C at 1 atm. The conversion of phenol and the selectivities to *o*-cresol and 2,6-xylenol are shown in Fig. 4. The conversion of phenol and the selectivity to 2,6-xylenol increased continuously with the increase of reaction temperature, while the selectivity to *o*-cresol decreased due to the series reaction. The conversion of phenol at 500°C was high as nearly 100% and the selectivity for 2,6-xylenol increased rapidly. It indicates that all phenols in the feed are converted into *o*-cresol and then the *o*-cresol into 2,6-xylenol. The early good catalytic performance was decreased rapidly at high reaction temperature.

The influence of the space velocity on the reaction was investigated by varying the feed rate over Mn–MgO catalyst at 460°C. The conversion of phenol and the selectivities were dependent on the feed rate as shown in Fig. 5. The conversion of phenol and the selectivity to 2,6-xylenol decreased as the space velocity increased, while the selectivity to *o*-cresol increased. It is considered that *o*-cresol is the primary product and 2,6-xylenol is the secondary product obtained from the alkylation of *o*-cresol. Thus, the increase of contact time gives less *o*-cresol but more 2,6-xylenol product. Fig. 6 shows the effect of the feed composition (MeOH/PhOH mole ratio) on the conversion and the product selectivities over Mn–MgO catalyst. The conversion of phenol and selectivity to 2,6-xylenol increased with the mole ratio of MeOH/PhOH.

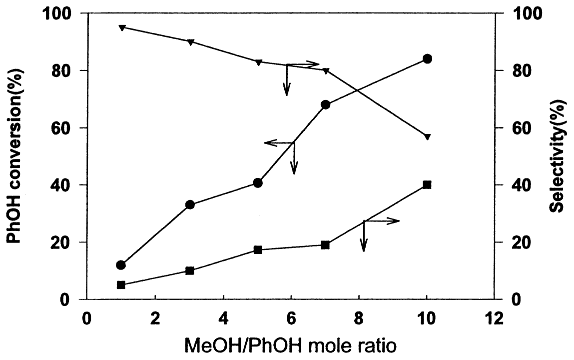

Fig. 6. Effect of feed molar ratio (MeOH/PhOH) on phenol conversion and product selectivities of Mn(2.5%)–MgO. Conversion of phenol (●) and selectivities to *o*-cresol (▼) and 2,6-xylenol (■). Reaction conditions are the same as Fig. 1 except for feed molar ratio.

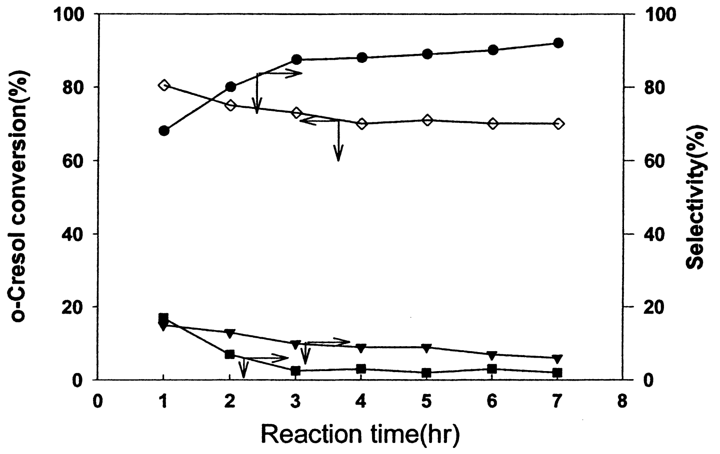

Fig. 7. Effect of *o*-cresol as feed on the activity and the product selectivities. Conversion of *o*-cresol (◇); 2,6-xylenol (●); 2,4,6-xylenol (▼); by-products (■). Reaction conditions: MeOH/*o*-cresol = 5/1; temperature = 460°C; catalyst = 0.2 g of Na–Mn–MgO; flow rate of N_2 carrier gas = 6 cc/min; liquid flow rate = 0.27 cc/min.

The results of alkylation using *o*-cresol as a reactant instead of phenol are shown in Fig. 7. The main product of *o*-cresol alkylation was 2,6-xylenol, whereas that of phenol alkylation was *o*-cresol. It suggests that phenol alkylation is proceeded by a series reaction (phenol → *o*-cresol → 2,6-xylenol → 2,4,6-trimethyl phenol (2,4,6-TMP)).

Table 3
Surface area and degree of deactivation over various catalysts[a]

Catalysts[b]	BET surface area (m^2/g)	PhOH conversion (%)	
		1 h	7 h
Mn(2.5)–MgO	170	40.6	30.7
Ga(2.5)–MgO		44.4	16.0
V(1)–MgO	165	58.4	32.7
V(2.5)–MgO	170	64.5	24.8
V(5)–MgO	169	62.5	14.8
Ni(3.5)–MgO	205	52.8	27.0
Co(1)–MgO		42.1	24.7
Cu(3.5)–MgO	247	59.9	25.2
Ga(2.5)–V(2.5)–MgO		37.2	5.0
V(1)–Mn(1)–MgO	216	76.0	31.0
Na(1)–Mn(1)–MgO[c]		30.0	27.0
Na(0.5)–Mn(1)–MgO[c]		28	20.7

[a] Reaction conditions are the same as in Table 1.

[b] The value in the parenthesis refers to mol%.

[c] Amount of catalyst = 0.2 g and flow rate of N_2 carrier gas = 6 cc/min.

3.4. Deactivation

The degree of deactivation and the surface areas of the catalysts are shown in Table 3. As mentioned earlier, the more acidic catalysts had higher activity, whereas the deactivation occurred rapidly during the reaction period. The surface areas of the catalysts after the reaction were in the range 165–250 m^2/g. A correlation between the surface area and the activity did not appear in this reaction.

Fig. 8 shows the thermal gravity analysis (TGA) thermogram of V–Mn–MgO catalyst reacted for vari-

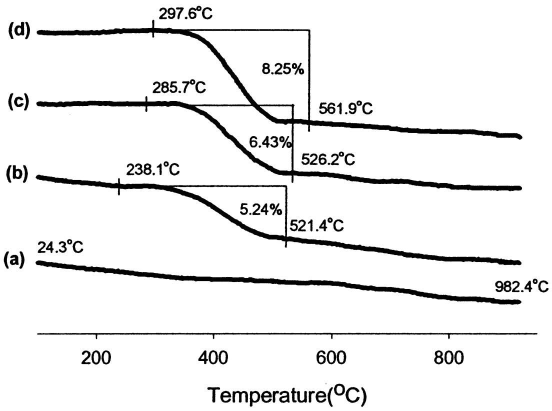

Fig. 8. TGA curves of V(2.5%)–Mn(1%)–MgO catalyst as reaction time: (a) fresh; (b) 1 h; (c) 7 h; (d) 14 h.

ous reaction times. As the reaction time increased, the temperature of the coke burn-off moved to higher temperatures and the deposition rate of coke increased. It indicates that the coke was deposited on acid sites and then, catalytic performance was decreased. The more deposits of coke formed a graphitic structure and it was more difficult to be removed by burning.

4. Conclusions

The alkylation of phenol with methanol over modified magnesium oxide catalysts can be summarized as follows:

1. Small amount of addition of dopants into the magnesium oxide was effective for the good balanced acid–base properties of the catalysts, and these gave better activity and the selectivity to 2,6-xylenol than the pure MgO catalyst.
2. The phenol conversion and the selectivities to *o*-cresol and 2,6-xylenol were maintained without the rapid change over Na(1%)–Mn(1%)–MgO catalyst, and the selectivity to *ortho*-alkylated products was very high. Sodium addition has a function in promoting the catalytic stability including good balanced acid–base property.
3. It is suggested that phenol alkylation is a series reaction (phenol → *o*-cresol → 2,6-xylenol → 2,4,6-TMP).
4. For V(2.5%)–Mn(1%)–MgO catalyst, catalytic performance was decreased because of the coke deposit on acid sites. The more deposits of coke formed a graphitic structure.

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