Ortho-alkylation of phenol derivatives with methanol over magnesium oxide catalysts. 1. Characterization of promoted magnesium oxide catalysts

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Received 2 January 2001; accepted 1 March 2001

Cr- and Pt-promoted magnesium oxide catalysts were used to catalyze *ortho*-alkylation of phenol derivatives in the presence of excess methanol. The characteristic properties of the MgO surface measured by XRD, SEM, BET, and TPD suggest that Cr exists as fine chromium oxide particles on the MgO surface, while a Pt and MgO interaction causes an increase of the BET surface area as well as of surface acid and base amounts. Cr/MgO shows a specialty for *ortho*-alkylation of phenol derivatives with methanol without forming O-alkylated products, i.e., anisole or methylated anisole. The catalytic activity and the stability of Cr/MgO are improved by the addition of a fairly small amount of Pt. The effect of Pt can be explained by the Pt and MgO interaction which increases both the acid and base amounts. A mechanism involving the reaction of phenol derivatives and methanol adsorbed simultaneously on acid–base pair sites is proposed.

KEY WORDS: *ortho*-alkylation; phenol; phenol derivatives; methanol; Cr/MgO; Pt–Cr/MgO

1. Introduction

Alkylation of phenol with methanol results in a range of products, some of them, such as anisole, *ortho*-cresol, *para*-cresol and 2,6-dimethylphenol, are extensively employed in industry. Anisole is an additive in gasoline to boost octane, *ortho*-cresol is an important organic intermediate for herbicides, and 2,6-dimethylphenol is useful as a starting material for the manufacture of polyphenylene oxide that is an important engineering plastic [1–4]. Currently, the industrial synthetic method is a liquid phase process [5,6], where phenol is methylated with methanol using an acid catalyst; however, this process not only needs a higher temperature but also produces a wide range of products including xylenol isomers, methylated cresol isomers and anisole. In previous works [7–9] we have found that 2,6-dimethylphenol can be synthesized selectively from cyclohexanol and/or cyclohexanone and methanol in one step over magnesium-oxide-supported chromium oxide catalysts that can be improved in catalytic activity by the addition of a fairly small amount of Pt ions. In an extension of this study of reaction kinetics, we have found that 2,6-dimethyl is formed via a phenol intermediate formed from cyclohexanol and/or cyclohexanone. These results prompted us to study the *ortho*-alkylation of phenol and phenol derivatives over Cr/MgO and Pt–Cr/MgO, respectively, using methanol as the methyl group source.

In this work, the character properties of Cr/MgO and Pt–Cr/MgO were measured by XRD, SEM, and TPD. The reactivities of a series of phenol derivatives, such as cresol isomers and xylenol isomers, with methanol over Cr/MgO and Pt–Cr/MgO were examined, respectively.

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2. Experimental

2.1. Preparation of catalysts

The Cr/MgO catalyst was prepared by impregnating magnesium oxide (MgO) with a solution containing chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$). The chromium content (wt%) was based on the concentration of the chromium ions in the processing solution. Impregnation took place in a water bath with stirring at 100 °C to evaporate excess water, and the cake was dried at 110 °C in an oven overnight. It was finally calcined by slowly heating (10 °C/min) to 500 °C in air and held for 6 h at the final temperature. The Pt–Cr/MgO catalyst was prepared by impregnating Cr/MgO with a solution containing platinum ions ($PtCl_4 \cdot 5H_2O$) in a similar method. The catalysts used in this study were Cr(2.5 wt%)/MgO and Pt(0.05 wt%)–Cr(2.5 wt%)/MgO.

2.2. Apparatus and procedure

The BET surface area of the catalysts was determined by N_2 adsorption at 77 K. The morphology of the MgO before and after loading Cr and/or Pt was observed using scanning electron microscopy (SEM). The observations were made with a Hitachi S800 microscope. X-ray diffraction (XRD) was performed with a Shimadzu XRD-6000 diffractometer. Catalyst samples (∼50 mg) were powdered, and the diffraction lines were measured with Cu K_α radiation.

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TPD experiments were carried out using a Micromeritics series 2900 spectrometer. A 20 mg sample was placed in a quartz TPD tube and pretreated at 400 °C in helium flow of 50 ml/min for 1 h. After cooling to 110 °C, adsorption of CO_2 (or pyridine) was carried out until saturated, then desorption proceeded from 110 to 800 °C at a rate of 10 °/min. The desorption was continuously monitored by a TCD detector.

The reaction of methanol and phenol was carried out in a continuous down flow fixed-bed reactor. The reactor was a vertical quartz tube with an inside diameter of 1.8 cm. It was heated by an electrical tubular furnace, and the temperature was controlled with a PID temperature controller with a sensor in the center of the catalyst bed. The catalyst (1 g) was packed in the reactor and pretreated at 500 °C in a stream of nitrogen (30 ml/min). After pretreatment, the catalytic reactions were carried out at 300–460 °C and 1 atm. The stream of feed was prepared as follows: a mixture of substrate (phenol or phenol derivatives) and methanol was fed by a syringe pump and vaporized in an evaporator. The vapor was adjusted to a constant rate of 15 ml/min and then diluted with nitrogen; the total flow rate was controlled at 45 ml/min, and the molar ratio of substrate to methanol in the feed was 1 : 10. The products were identified by gas chromatography–mass spectrometry and were analyzed quantitatively with a gas chromatograph attached to the reaction system through a gas-sampling valve. The columns used in the gas chromatograph were a SP2100 column (3 m) and a Chroseive II column for H_2, CO and CO_2 analysis.

3. Results and discussion

3.1. Characterization of catalysts

The XRD patterns of MgO with Cr and/or Pt promoters are illustrated in figure 1. The characteristic peaks of MgO remain unchanged before and after the addition of chromium oxide indicating that the MgO structure has not been changed, and further, the chromium oxide diffraction peaks are not found, even though at higher Cr content (10 wt%), but the Cr/MgO catalyst has a color similar to chromium oxide. These results suggest that Cr exists on the MgO surface as very fine chromium oxide particles not to be detected by XRD. Surprisingly, when a very small amount (0.05 wt%) of Pt ions are added to the Cr/MgO catalyst, the XRD pattern of the Pt–Cr/MgO catalyst gives new peaks which are markedly different from the patterns taken with MgO or Cr/MgO, but similar to the pattern taken with Pt/MgO, which is indicative of a Pt-doping effect causing the evolution of new crystalline planes. Since the radius of a Pt^{2+} ion (0.052 nm) is smaller than that of a Mg^{2+} ion (0.065 nm), the Pt^{2+} ions may fit into the MgO lattice and thus cause a structure distortion.

The effects of the addition of Pt to Cr/MgO also appear in the BET surface area and the SEM image changes. The BET surface areas of various MgO catalysts are summarized

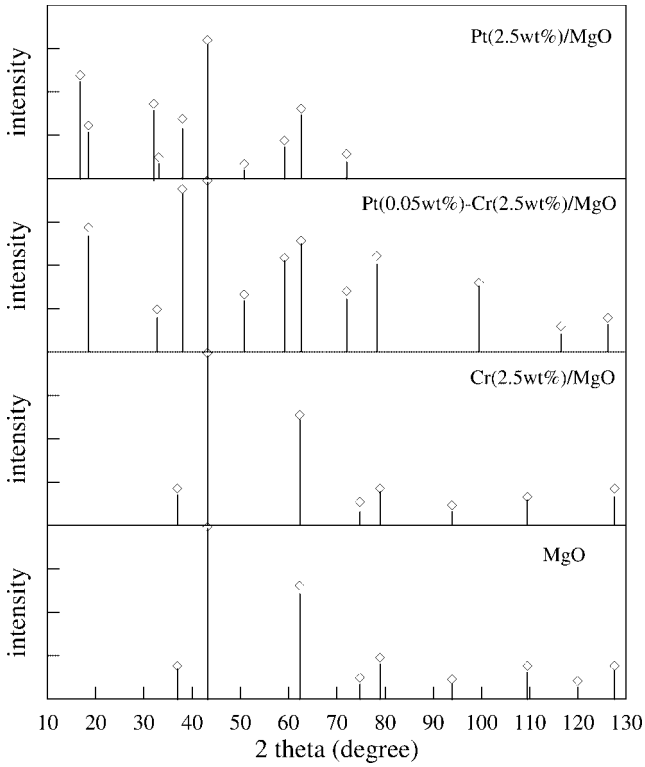

Figure 1. The XRD patterns of various prompted magnesium oxide catalysts.

Table 1
The BET surface area for catalysts.

Catalyst	BET surface area (m^2/g)
MgO	39
Cr(2.5 wt%)/MgO	46
Pt(0.05 wt%)–Cr(2.5 wt%)/MgO	114
Pt(2.5 wt%)/MgO	110

in table 1. Magnesium oxide (MgO, Merck), the support, has a surface area of about 40 m^2/g before and after calcination at 500 °C. The BET surface area increases to about 50 m^2/g as chromium oxide is loaded on MgO, and further increases to about 100 m^2/g as the Cr/MgO is modified by the addition of Pt ions. In addition, in the absence of chromium oxide, the addition of Pt ions also causes an increase of the BET surface area of MgO from about 40 to 110 m^2/g.

The SEM prints of various MgO catalysts are illustrated in figure 2. By comparing the SEM prints, we have found that the MgO surface structure has not been changed markedly after addition of chromium oxide. In contrast, Pt–Cr/MgO has a SEM print different from that of MgO and Cr/MgO, but similar to the SEM print of Pt/MgO, which is indicative of a Pt and MgO interaction on the MgO surface.

CO_2 TPD profiles of MgO, Cr/MgO and Pt–Cr/MgO catalysts are illustrated in figure 3. By comparison, the area under the profiles, the CO_2 TPD profile of MgO shows two broad desorption peaks at 180 and 280 °C, while as Cr is

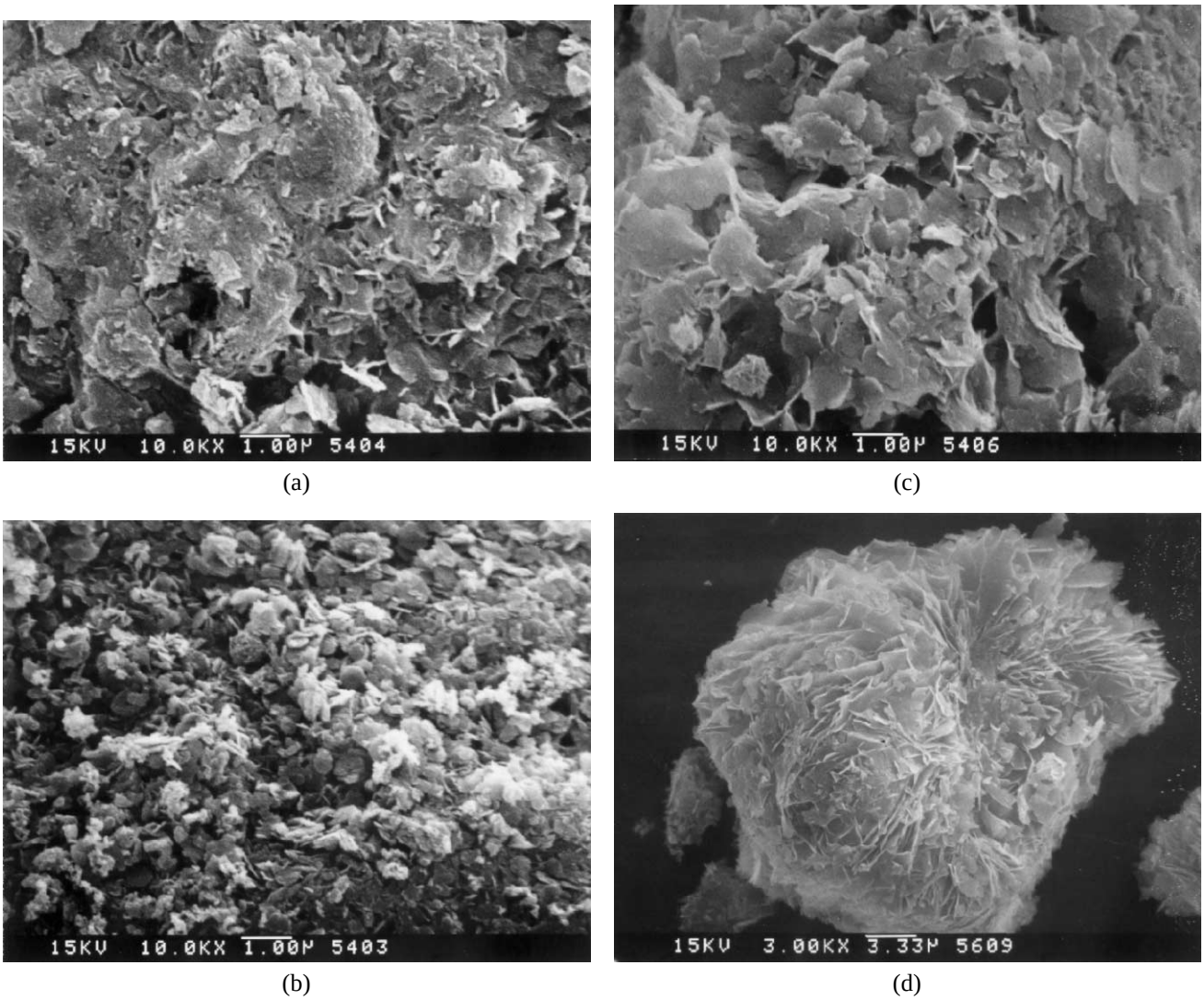

Figure 2. SEM prints of various promoted MgO catalysts: (a) MgO, (b) Cr/MgO, (c) Pt–Cr/MgO, and (d) Pt/MgO.

loaded on MgO, the desorption peaks in intensity as well as the area under the CO_2 TPD profile decrease. As Pt is added on Cr/MgO, the area under the CO_2 TPD profile increases, indicating that the base amount increases but the base strength is not changed significantly.

Pyridine TPD profiles of MgO, Cr/MgO and Pt–Cr/MgO catalysts are shown in figure 4. The TPD profile of MgO shows two peaks at 200 and 280 °C, respectively. When Cr is loaded on MgO, the area under the 280 °C peak decreases and the area under the 200 °C peak increases, indicating that the strong acid sites are destroyed but the amount of weak acid sites increases. And further, when Pt is loaded on Cr/MgO, the base amount increases significantly. The results suggest the existence of chromium oxide fine particles on the MgO surface as described previously, which may cover the MgO surface and cause a decrease of base amounts; while the chromium oxide, possessing a weak acidity, so causes the profile area of Cr/MgO to increase at lower temperatures. The Pt–MgO interaction causes both the acid and base amounts to increase.

3.2. Reactions of phenol derivatives and methanol over Cr/MgO and Pt–Cr/MgO

The results of the alkylation of phenol and various mono and dimethylphenols with methanol over Cr/MgO after reaction for 2 h are summarized in table 2. The reaction of phenol and methanol yields 2-methylphenol (*ortho*-cresol) and 2,6-dimethylphenol (2,6-DMP) (run 1). According to the stoichiometry for the formation of *ortho*-cresol and 2,6-DMP from phenol and methanol, *ortho*-cresol is a primary product that formed by the addition of a methyl group to phenol, therefore, 2,6-DMP is a secondary product formed by the further reaction of *ortho*-cresol with methanol. The ratio of the secondary product to the primary product is about 1 : 4.

Instead of phenol, when monomethylphenols (*ortho*-, *meta*-, and *para*-cresol) are used in the reaction, DMP and trimethylphenol (TMP) become a primary product and secondary product, respectively. All the conversions of these cresols are higher than those of phenol (runs 2–4) suggest-

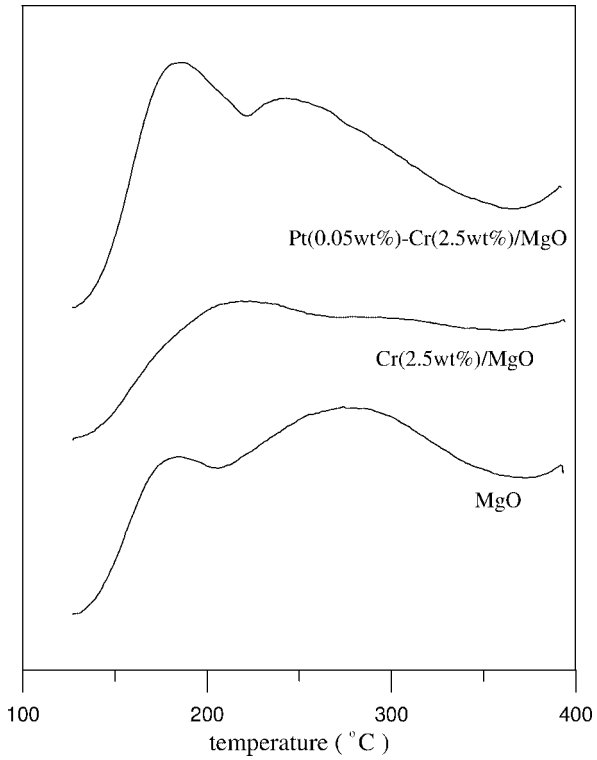

Figure 3. CO_2 TPD profiles of various promoted magnesium oxide catalysts.

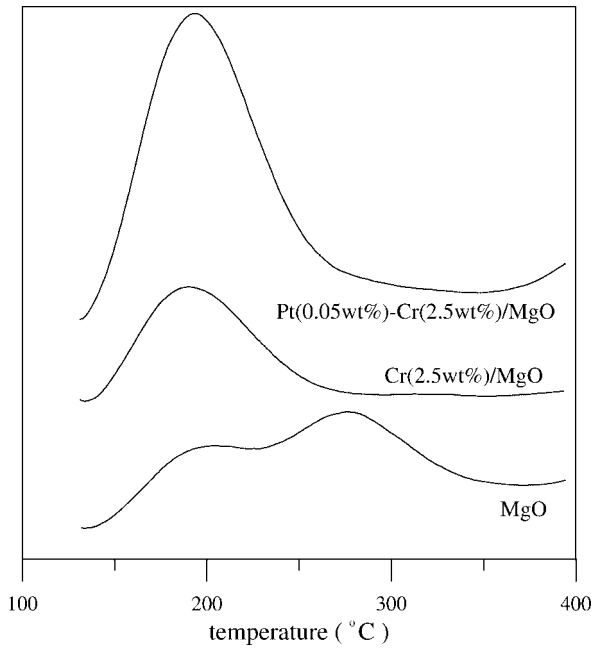

Figure 4. Pyridine TPD spectra of various promoted magnesium oxide catalysts.

ing that the existence of a methyl group on the benzene ring of phenol increases the reactivity of phenol. In the reaction of *ortho*-cresol and methanol, the reaction yields 2,6-dimethylphenol (2,6-DMP) as main product with a fairly small amount of 2,4,6-trimethylphenol (2,4,6-TMP) (run 2), thus the ratio of the secondary product to the primary product becomes very small, indicating that the secondary product is hard to be formed. In contrast, when instead of *ortho*-cresol *meta*-cresol is used in the reaction, the ratio of the secondary product (2,3,6-TMP) to the primary product (2,5-DMP + 2,3-DMP) increases to about 1 : 2 (run 3), as well as in the reaction of *para*-cresol and methanol, which shows a similar value in the ratio of secondary product (2,4,6-TMP) to the primary product (2,4-DMP) (run 4). The results suggest that the alkylation of phenol derivatives with methanol over Cr/MgO is limited to the *ortho*-positions of the phenol skeleton. According to the results for the methylation of phenol to give 2,6-DMP, which indicate that phenol is adsorbed on the catalyst as phenolate ion, such that the *ortho*-positions are very near to the catalyst surface, hence only the *ortho*-positions can be methylated [10]. By analogy, in the reaction of cresol and methanol, the *ortho*-selectivity of the Cr/MgO catalyst can be attributed to the nature of adsorption of cresol on the catalyst.

Table 2
Conversion and selectivity data for the reaction of various substrates with substrate : methanol = 1 : 10 at 1 atm and 440 °C catalyzed by Cr(2.5 wt%)/MgO.

Run	Substrate	Conv. (%)	Selectivity[a] (%)			
			DMP	TMP	TetraMP	Others
1	Phenol	26.0	18.6 (2,6)	–	–	81.4 (2,4,6)
2	*o*-cresol	74.3	97.2 (2,6)	2.8 (2,4,6)	–	–
3	*m*-cresol	56.4	53.9 + 14.9 (2,5 + 2,3)	31.2 (2,3,6)	–	–
4	*p*-cresol	44.1	69.0 (2,4)	27.7 (2,4,6)	–	3.3
5	2,3-DMP	68.5	–	100 (2,3,6)	–	–
6	2,4-DMP	56.5	–	92.0 (2,4,6)	–	8.0
7	2,5-DMP	78.3	–	100 (2,3,6)	–	–
8	3,4-DMP	60	–	62.0 (2,3,4)	38.0 (2,3,4,6)	–
9	3,5-DMP	50.4	–	74.2 (2,3,5)	25.8 (2,3,5,6)	–
10	2,6-DMP	9.0	–	100 (2,4,6)	–	–

[a] The numbers in the parentheses indicate the locations of methyl groups.

To verify the postulation that the alkylation of phenol derivatives over Cr/MgO occurs at *ortho*-positions, we further examined the reactions using various dimethylphenol (DMP) isomers including 2,3-, 2,4-, 2,5-, 3,4-, 3,5-, and 2,6-DMP. Results are also given in table 2 (runs 4–10). According to the positions of methyl groups on the benzene ring of phenol, these DMP isomers may be distinguished into three groups. The first group, 2,3-, 2,4-, and 2,5-DMP have an *ortho*-position vacancy on the benzene ring. The second group, 3,4- and 3,5-DMP, possesses double vacancies of *ortho*-positions. Furthermore, 2,6-DMP is a reactant without *ortho*-position vacancy. The alkylations of 2,3-, 2,4-, and 2,5-DMP with methanol, selectively yield corresponding *ortho*-methylated products (2,3,6-, 2,4,6-, and 2,3,6-TMP), re-

Table 3
Conversion and selectivity data for the reaction of various substrates with substrate : methanol = 1 : 10 at 1 atm and 440 °C catalyzed by Pt(0.05 wt%)–Cr(2.5 wt%)/MgO.

Run	Substrate	Conv. (%)	Selectivity[a] (%)			
			DMP	TMP	TetraMP	Others
1	Phenol	75.3	65.1 (2,6)	–	–	34.9 (2,4,6)
2	*o*-cresol	93.0	88.3 (2,6)	11.7 (2,4,6)	–	–
3	*m*-cresol	79.4	60.7 + 5.1 (2,5 + 2,3)	28.8 (2,3,6)	–	5.4
4	*p*-cresol	73.2	43.9 (2,4)	52.8 (2,4,6)	–	3.3
5	2,3-DMP	88.6	–	87.1 (2,3,6)	–	13.9
6	2,4-DMP	86.7	–	90.3 (2,4,6)	–	9.7
7	2,5-DMP	88.3	–	90.7 (2,3,6)	–	9.3
8	3,4-DMP	88.8	–	33.9 (2,3,4)	66.1 (2,3,4,6)	–
9	3,5-DMP	93.4	–	11 (2,3,5)	89 (2,3,5,6)	–
10	2,6-DMP	22.7	–	100 (2,4,6)	–	–

[a] The numbers in the parentheses indicate the locations of methyl groups.

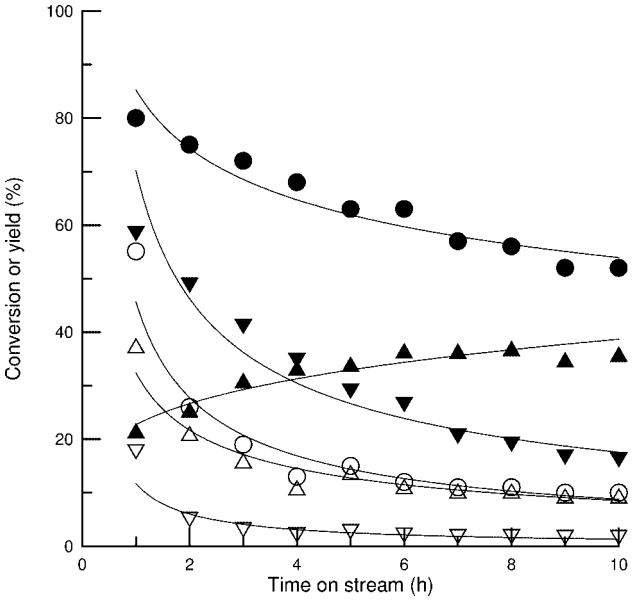

Figure 5. Variation of phenol conversion and yields of products with time on stream in the reaction of phenol and methanol (1 : 10) over Cr/MgO and Pt–Cr/MgO at 440 °C; (○) phenol conversion, (△) *ortho*-cresol, and (▽) 2,6-DMP; open symbols for Cr/MgO and filled symbols for Pt–Cr/MgO.

spectively (runs 5–7). While, the reaction of 3,4-DMP and methanol yields 2,3,4-TMP and 2,3,4,6-TetraMP (run 8), as well as, the reaction of 3,5-DMP and methanol yields 2,3,5-TMP and 2,3,5,6-TetraMP (run 9). Either 3,4- or 3,5-DMP, which have double *ortho*-position vacancies, is used as the starting material. The reaction gives a value of about 1 : 2 for the ratio of TetraMP to TMP, similar to the result given in the reaction of phenol and methanol. As postulated, 2,6-DMP shows a very poor reactivity (run 10), owing to the fact that the *ortho*-positions of phenol are already occupied by methyl groups. These results show the specialty of Cr/MgO that catalyzed the *ortho*-alkylation of phenol derivatives with methanol.

The activity of the Cr/MgO catalyst for the *ortho*-alkylation of phenol derivatives is improved by the addition of platinum (Pt–Cr/MgO). The results of the alkylation of phenol and various mono and dimethylphenols with methanol over Pt–Cr/MgO are summarized in table 3. By comparing with table 2, all the conversions over Pt–Cr/MgO are higher than that over Cr/MgO. In the reactions of phenol and phenol derivatives that have double *ortho*-position vacancies, i.e., *meta*-cresol, *para*-cresol, 3,4-DMP and 3,5-DMP, with methanol, the yields of corresponding secondary products (2,3,6-TMP, 2,4,6-TMP, 2,3,4,6-TetraMP, and 2,3,5,6-TetraMP) increase remarkably, and therefore the ratio of secondary product to primary product increases from 1 : 2 to 2 : 1 (runs 1, 3, 4, 8, and 9). In contrast, the reactions of *ortho*-cresol and various DMP isomers with one *ortho*-position vacancy, i.e., 2,3-, 2,4-, and 2,5-DMP with methanol, yield monomethylated products (2,6-DMP, 2,3,6-TMP, 2,4,6-TMP, and 2,3,6-TMP) as main products, respectively (runs 2, 5, 6 and 7). The 2,6-DMP still shows very poor reactivity (run 10). The results suggest that the addition of Pt increases the methylation activity of Cr/MgO, but does not alter the specialty of Cr/MgO for *ortho*-methylation with methanol.

Figure 5 shows the phenol conversions and the yields of *ortho*-cresol and 2,6-DMP as a function of time in the reaction of phenol and methanol (molar ratio phenol/methanol = 1/10) at 440 °C over Cr(2.5 wt%)/MgO and Pt(0.05 wt%)–Cr(2.5 wt%)/MgO (1 g), respectively. Cr/MgO has an initial activity comparable to Pt–Cr/MgO, but the activity of Cr/MgO decays faster than that of Pt–Cr/MgO. The fresh Cr/MgO shows an activity (appears in conversion and selectivity) similar to Pt–Cr/MgO that has been performed for 10 h, indicating that the product distribution is a function of conversion. The phenomena also have been found in the reactions of phenol derivatives and methanol. Typically, the reaction of *ortho*-cresol and methanol and the reaction of 2,5-DMP and methanol are illustrated in figures 6 and 7, respectively. Among the reactions, there is a rapid deactivation for phenol; the deactivation rate decreases as the number of methyl groups in the reactant increases. The rapid deactivation of phenol can be ascribed to the stronger acidity of phenol than that of mono or dimethylphenol, since the acidity is weakened by the presence of alkyl groups in the benzene ring. In a separate experiment, it was also found that the mole ratio of methanol to phenol lower than 5 caused a rapid deactivation of the catalysts. It is noteworthy that no O-alkylated product such as anisole or methylated anisole is detected in the reactions over Cr/MgO or Pt–Cr/MgO even at very low conversions.

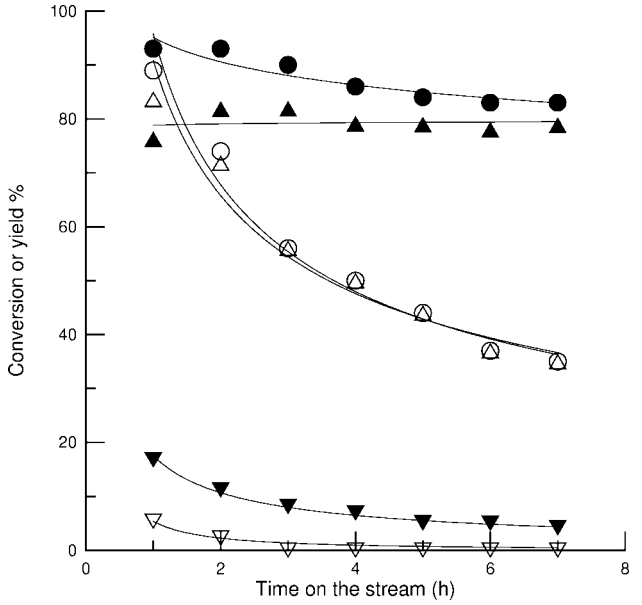

Figure 6. Variation of *ortho*-cresol conversion and yields of products with time on stream in the reaction of *ortho*-cresol and methanol (1 : 10) over Cr/MgO and Pt–Cr/MgO at 440 °C; (○) *ortho*-cresol conversion, (△) 2,6-DMP, and (▽) 2,4,6-TMP; open symbols for Cr/MgO and filled symbols for Pt–Cr/MgO.

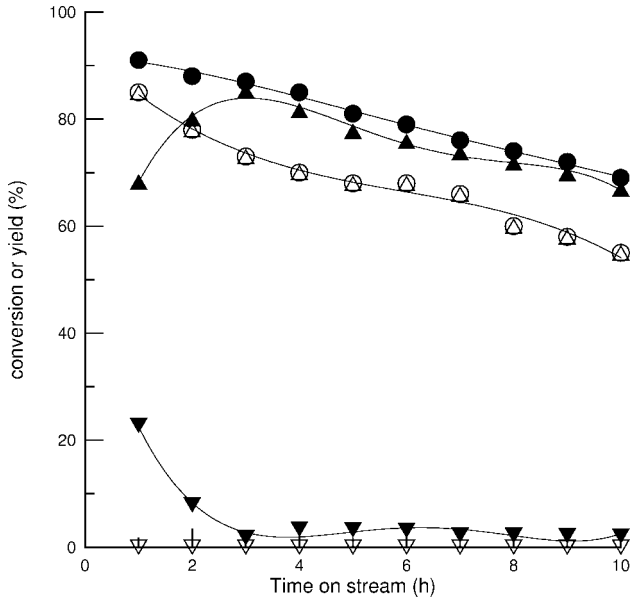

Figure 7. Variation of 2,5-DMP conversion and yields of products with time on stream in the reaction of 2,5-DMP and methanol (1 : 10) over Cr/MgO and Pt–Cr/MgO at 440 °C; (○) 2,5-DMP conversion, (△) 2,3,6-TMP, and (▽) 2,3,4,6-TetraMP; open symbols for Cr/MgO and filled symbols for Pt–Cr/MgO.

3.3. Proposed mechanism for the reaction of phenol derivatives and methanol over magnesium oxide catalysts

It was reported that solid acid or solid base catalysts could be used to catalyze alkylation of phenol with methanol [10]. With acid catalysts such as zeolites [11–13] and Nafion H [14], methanol molecule is chemisorbed on an acid center of the catalyst with methyoxonium ion formation, and then a gaseous phenol molecule reacts with adsorbed methanol giving products. However, the O-alkylation product, i.e., anisole, is also produced simultaneously in addition to C-alkylation products such as cresol and xylenol. Especially, O-alkylated products are the main products at low conversion, indicating that the selectivity is a function of conversion for the acid catalyst. For catalysts of basic properties, such as MgO for example, it is the phenol molecule that is activated to form phenolate anion capable of reacting with methanol, giving products of O- and C-alkylation with selectivity depending on the conversion of phenol, while high selectivity to anisole over basic Cs ion exchanged zeolite is no more a function of conversion [15].

We found no O-alkylated product formed in the reaction of phenol derivative and methanol over Cr/MgO or Pt–Cr/MgO, which is different from that of the phenol methylation catalyzed by simple solid acid or base. The results of pyridine TPD and CO_2 TPD, which indicate that Cr/MgO possesses simultaneously acidic and basic centers, and both the acid and the base amounts but strength increase as Pt is added on Cr/MgO, with the increase of Cr/MgO activity by the addition of Pt for the reaction of phenol derivative and methanol, one can assume that active center is an acid–base pair site.

Reacting species, phenol derivative and methanol are chemisorbed and thus activated. Methanol activation leading to CH_3^+ cation is possible on acid sites; phenol is adsorbed on the catalyst base site as phenolate ion, such that the *ortho*-positions are very near to the catalyst surface and hence only the *ortho*-positions can be methylated.

4. Conclusion

The Cr- and Pt-promoted magnesium oxide catalysts catalyzed *ortho*-alkylation of phenol derivatives with methanol. Cr/MgO shows a specialty for *ortho*-alkylation of phenol derivatives with methanol without forming O-alkylated products. The catalytic activity and the stability of Cr/MgO are improved by the addition of a fairly small amount of Pt. XRD, SEM, and TPD experiments show that Cr exists as fine chromium oxide particles on the MgO surface, while a Pt and MgO interaction causes the BET surface area as well as surface acid and base amounts to increase, which leads to increased activity of the catalyst. A mechanism involving the reaction of the phenol derivative and methanol adsorbed simultaneously on acid–base pair sites is proposed.

Acknowledgement

Financial support by National Science Council (NSC 89-2113-M-126-003) is gratefully acknowledged.

References

[1] H. Nakajima, F. Nomura and S. Iszwa, US Patent 3 855 318 (1974), to Asahi Kasei Kabushiki Kaisha.

[2] H. Fiege and Ulmann, in: *Encyclopedia of Industrial Chemistry*, Vol. A8, eds. W. Gerhartz, Y.S. Yamamoto, F.T. Campbell, R. Pfefferkorn and J.F. Rounsaville (VCH, Weinheim, 1987) ch. 1.

[3] V.V. Rao, V. Durgakumari and S. Narayanan, Appl. Catal. 49 (1989) 165.

[4] S. Velu and C.S. Swamy, Appl. Catal. A 119 (1994) 241.

[5] B.L. Leach, US Patent 3 994 982 (1976), to Continental Oil.

[6] M. Kiawamata, K. Ohshima, A. Kudoh, M. Kotani, US Patent 4 208 537 (1980), to Mitsui Toatsu Chemicals.

[7] F.L. Wang, T.F. Tsai, Y.H. Tsai and Y.K. Cheng, Appl. Catal. A 126 (1995) 229.

[8] F.L. Wang and T.F. Tsai, Catal. Today 44 (1998) 259.

[9] F.L. Wang and T.F. Tsai, J. Chinese Chem. Soc. 47 (2000) 163.

[10] K. Tanabe, in: *Studies in Surface Science and Catalysis*, Vol. 20, eds. B. Imelik, C. Naccache, G. Coudurier, Y.B. Taarit and J.C. Vedrine (Elsevier, Amsterdam, 1985) ch. 1.

[11] M. Marczewski, G. Perot and M. Guisnet, *Studies in Surface Science and Catalysis* (Elsevier, Amsterdam 1988).

[12] M. Marczewski, J.P. Bodibo, G. Perot and M. Guisnet, J. Mol. Catal. 50 (1989) 211.

[13] E. Santacesaria, M. DiSeria and P. Ciambelli, Appl. Catal. 64 (1990) 101.

[14] J. Caspi and G.A. Olar, J. Org. Chem. 43 (1978) 3142.

[15] S.C. Lee, S.W. Lee, K.S. Kim, T.J. Lee, D.H. Kim and J.C. Kim, Catal. Today 44 (1998) 253.