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Catalytic synthesis of 2,6-dimethylphenol from methanol and KA-oil over magnesium oxide catalysts

Fey-long Wang*, Tan-feng Tsai

Department of Applied Chemistry, Providence University, Sha-Lu, Taichung Hsien, 43301 Taiwan, Taiwan

Abstract

Catalytic synthesis of 2,6-dimethylphenol from methanol and KA-oil (mixture of cyclohexanol and cyclohexanone) was achieved by using magnesium oxide-supported chromium oxide catalysts in one step. The activity of Cr/MgO catalysts depended on the concentration of chromium. At high conversion (>90%), dimethylphenol was formed in high yield (>60%) with minor amounts of methylated cyclohexanol and/or cyclohexanone, which may further be reacted to form the desired product. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

2,6-Dimethylphenol is useful as a starting material for the manufacture of polyphenylene oxide, an important engineering plastic [1]. Currently, the industrial synthetic method is a liquid-phase process, where phenol is methylated with methanol using an Al_2O_3 catalyst; however, this process not only needs a high pressure and temperature but also produces a wide range of products, including various isomers of xylenol [2,3]. We have recently developed a new catalytic method for selectively synthesizing 2,6-dimethylphenol from methanol and cyclohexanone in one step over titanium oxide-supported vanadium oxide catalyst [4]. In an extension of this study, we have also found that 2,6-dimethylphenol may be synthesized from methanol and cyclohexanol selectively [5]. In addition, the commercially favored route to adipic acid is the oxidation cleavage of cyclohexane, which is a two-stage process with the intermediates cyclohexanol/cyclohexanone (KA-oil) [6]. These results prompted us to study the reaction of KA-oil and methanol for the formation of 2,6-dimethylphenol.

2. Experimental

2.1. Catalyst preparation

All chemicals used were of reagent grade quality and were commercially available. Supported catalysts were prepared by a simple impregnation method. Catalysts containing 2.5% chromium by weight were prepared as follows. To 1 l of deionized water containing 1.924 g chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$), 10 g of desired support was then slurried in the solution. Impregnation took place on 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 holding for 6 h at the final temperature. Other

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*Corresponding author. Tel.: 00 886 4 6310631; fax: 00 886 4 6311170; e-mail: flwang@simon.pu.edu.tw

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Table 1
The BET surface area for catalysts

Catalyst	BET surface area (m^2/g)
MgO	39
Cr(0.1 wt%)/MgO	49
Cr(1 wt%)/MgO	45
Cr(2.5 wt%)/MgO	46
Cr(8 wt%)/MgO	42
Cr(10 wt%)/MgO	46
Cr(12 wt%)/MgO	49

catalysts that contain different amounts of chromium were prepared in a similar manner, but the metal contents were controlled by adding the required amount of $Cr(NO_3)_3 \cdot 9H_2O$ in the prepared solution. The main catalysts used in this study were the magnesium oxide-supported chromium oxide catalysts (Cr/MgO). Magnesium oxide, the support, had a BET surface area of about 40 m^2/g before and after calcination at 500°C. As chromium oxide was loaded on MgO, the BET surface area increased to about 50 m^2/g, but the increments of that were not dependent upon the Cr content in Cr/MgO (Table 1). The XRD spectra of various Cr/MgO samples are illustrated in Fig. 1. The spectra indicate that MgO structure had not been changed after treatment.

2.2. Reaction apparatus and procedure

The reactions of methanol and KA-oil were 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 400°C in a stream of nitrogen (30 ml/min). After pretreatment, the catalytic reactions were carried out with a WHSV of 0.4 (g of feed/h g of catalyst) at 350–400°C and 1 atm. The stream of feed was prepared as follows: a

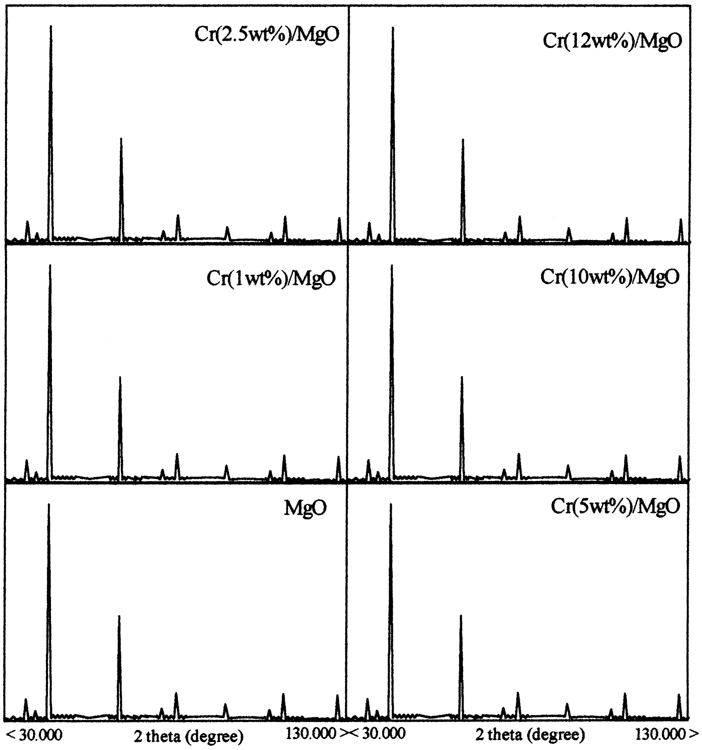

Fig. 1. X-ray diffraction patterns of MgO and Cr/MgO catalysts.

mixture of KA-oil 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. Unless otherwise indicated, the mole ratio of KA-oil to methanol in the feed was 1:10, and the mole ratio of cyclohexanol to cyclohexanone in KA-oil was 1:1. The products were identified by gas chromatography-mass spectrometry and analyzed quantitatively with a gas chromatography attached to the reaction system through a gas-sampling valve. The columns used in the gas chromatography were a FFAP column (3 m) at 110–200°C (25°C/min ramp) and a Chromseive II column at room temperature for H_2, CO and CO_2 analysis.

TPR experiments were carried out using a Micromeritics series 2900 spectrometer. A 20 mg sample was placed in a quartz TPR tube and pretreated at 400°C in helium flow of 50 ml/min for 1 h. After cooling to 20°C, the TPR measurement was effected by heating to 88°C at a rate 20°C/min, in a flow containing 95% argon and 5% hydrogen of 30 ml/min. The consumption of hydrogen was continuously monitored by a TCD detector.

Fourier transform infrared spectra of surface species were recorded with a Perkin-Elmer system 2000 FT-IR instrument having a spectral resolution of 4 cm^{-1}. A Harrick Scientific evacuable diffuse reflection accessory (DRA) (model HVC-DR2) was employed as a reactor. K type thermocouples were used for temperature measurements, and the catalyst temperature was controlled using an automatic temperature controller (Harrick Model ATC-30D). Catalyst samples diluted with a KBr powder in a ratio of 1:15 were in situ calcined at 400°C for 1 h under evacuation (10^{-2}–10^{-3} Torr). After this pretreatment, the samples were cooled to 25°C under evacuation for other treatments and measurements.

3. Results and discussion

3.1. Activities of bare supports

ZrO_2, WO_3, Al_2O_3, Mn_2O_3, Mn_3O_4 and MgO maintained a stable activity for KA-oil conversion and a stable selectivity lasting a few hours, while as CaO, ZnO, Fe_2O_3 and TiO_2 were used, the conversion and the selectivity varied with time, and steady state was not obtained. For the comparison, results at the second hour are summarized in Table 2. According to the product distributions, these metal oxides may be distinguished into three groups. The first group, CaO, WO_3, and Al_2O_3, merely catalyzed the dehydration reaction of the reactants and produced gases, such as cyclohexane, cyclohexene and light hydrocarbons, as main products. The second group, ZnO, Fe_2O_3, Mn_2O_3 and Mn_3O_4, showed activity that catalyzed the alkylation of KA-oil with methanol to form methylcyclohexanone, dimethylcyclohexanone, etc. Furthermore, ZrO_2, TiO_2 and MgO showed both alkylation and ring-dehydrogenation activities for

Table 2
Conversion and selectivity data for KA-oil reaction with WHSV=0.4 h^{-1} and methanol:KA-oil=10:1 at 1 atm and 400°C catalyzed by metal oxide catalysts

Metal oxide	Conversion	Selectivity(%)					
		me- & dime-Cyclohexanone	me- & dime-Cyclohexen-1-one	me-Cyclohexanol	2,6-DMP	2,4,6-TMP	Gases
CaO	1.4	0.0	0.0	0.0	0.0	0.0	100.0
WO_3	16.5	0.0	0.0	0.0	31.0	15.5	53.6
Al_2O_3	3.3	0.0	0.0	54.4	0.0	0.0	45.6
ZnO	56.2	24.5	34.6	23.6	8.0	2.2	7.2
Fe_2O_3	86.9	55.7	12.9	6.2	20.6	2.9	1.8
Mn_2O_3	63.6	55.0	31.9	4.1	3.5	0.7	4.8
Mn_3O_4	65.0	55.5	5.6	26.3	3.0	0.4	9.2
ZrO_2	85.2	11.7	22.2	3.4	36.8	4.8	21.1
TiO_2	12.2	11.2	18.1	22.0	20.3	4.5	24.0
MgO	56.2	23.6	7.5	40.1	17.4	7.4	3.9

the formation of 2,6-dimethylphenol from KA-oil and methanol. Except for Mn_3O_4, Al_2O_3 and MgO, the ratio of cyclohexanol to cyclohexanone in recovered KA-oil is less than 1, and the products are rich in methylated cyclohexanone for almost all metal oxides tested after the reaction. The results agree well with those of thermodynamic calculations which show that cyclohexanone is favored in the system containing cyclohexanol and cyclohexanone at higher temperature. These results suggest that cyclohexanol is easily converted to cyclohexanone in this reaction. However, it is interesting that MgO is able not only to maintain the hydroxide group of cyclohexanol but also to form methylcyclohexanol as the main product in the reaction.

3.2. Activities of magnesium oxide-supported catalysts

Results of the reaction over various magnesium oxide-supported metal oxides are given in Table 3. The activity of magnesium oxide was improved by loading metal oxides on its surface. As seen in the table, magnesium oxide-supported chromium (Cr/MgO) exhibited the most promising characteristics in the catalytic synthesis of 2,6-dimethylphenol (2,6-DMP). In addition, we have also found that, except for magnesium oxide, chromium oxide loaded on any other metal oxide that appears in Table 2 cannot enhance the characteristic activity for the formation of 2,6-DMP from the reaction of methanol and KA-oil. So far, Cr and MgO are the best combination for the reaction.

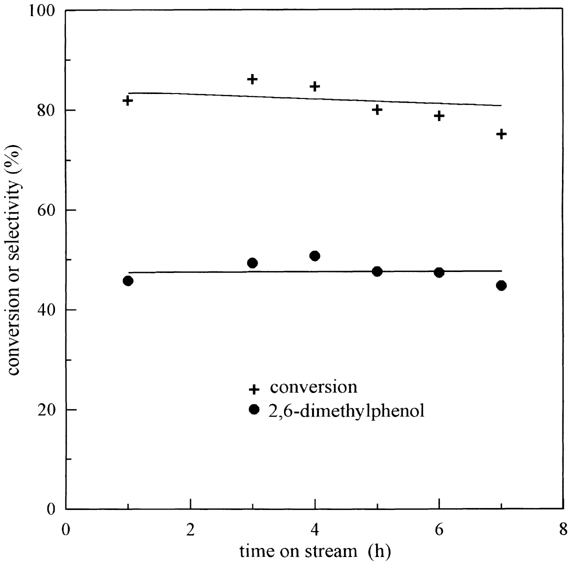

Fig. 2. KA-oil conversion and selectivity to 2,6-dimethylphenol versus time on stream over Cr(2.5 wt%)/MgO at 400°C.

Fig. 2 shows the KA-oil conversion and the selectivity to 2,6-DMP as a function of time in the reaction of KA-oil and methanol (mole ratio: cyclohexanol:cyclohexanone:methanol=0.5:0.5:10) over Cr(2.5 wt%)/MgO catalyst (1 g) at 400°C. The reaction yields methylated phenol, including 2,6-DMP and 2,4,6-trimethylphenol (2,4,6-TMP), methylated cyclohexanol (2-methylcyclohexanol and 2,6-dimethylcyclohexanol), methylated cyclohexanone (2-methylcyclohexanone and 2,6-dimethylcyclohexanone), and small amounts of phenol. Excess methanol

Table 3
KA-oil reaction with WHSV=0.4 h^{-1} and methanol:KA-oil=10:1 at 1 atm and 400°C catalyzed by magnesium oxide-supported catalysts

Metal	Conversion	Selectivity(%)					
		me- & dime-Cyclohexanone	me- & dime-Cyclohexen-1-one	me-Cyclohexanol	2,6-DMP	2,4,6-TMP	Gases
Ti	100.0	0.0	0.0	0.0	14.4	1.5	84.0
V	78.2	41.2	9.3	11.2	29.5	6.4	2.4
Cr	89.8	9.3	4.0	11.9	52.4	20.5	1.9
Mn	45.4	38.7	3.0	46.5	11.9	0.0	0.0
Fe	56.0	30.7	9.5	24.2	20.8	11.0	3.9
Co	42.4	34.1	24.5	36.7	0.0	0.0	4.8
Ni	73.4	32.3	14.4	47.0	0.0	0.0	6.4
Cu	39.0	47.0	4.9	48.1	0.0	0.0	0.0
Zn	51.2	35.6	7.9	43.8	2.9	5.2	4.5

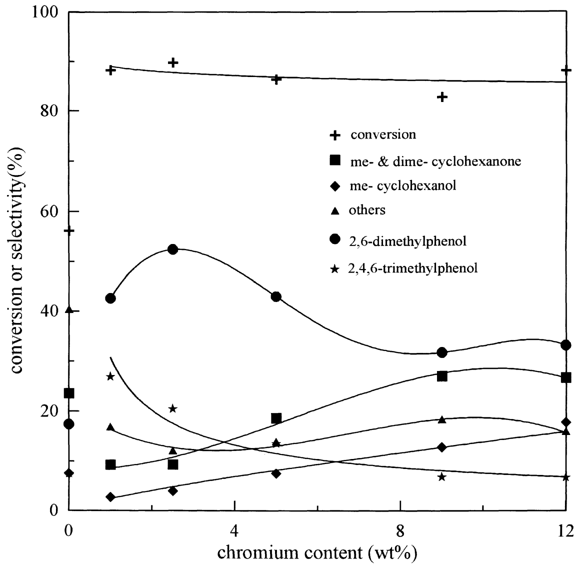

Fig. 3. Addition effect of Cr to MgO on the reaction of KA-oil and methanol at 400°C, 1 atm, and methanol/KA-oil (mol)=10.

was recovered after the reaction in addition to trace amounts of methane. The activity decreased slightly with time, and so on the other Cr(× wt%)/MgO catalysts, and at different reaction conditions.

The activities of Cr/MgO catalysts strongly depend on the concentration of chromium. The dependencies of KA-oil conversion and selectivity on the chromium content are shown in Fig. 3. The catalyst properties can be enhanced only by the addition of a fairly small amount of chromium, and excess addition results in a decrease in activity and selectivity to 2,6-DMP. At higher Cr loadings, catalysts show lower activities for the formation of 2,6-DMP, but produce methylated cyclohexanol and methylated cyclohexanone as main products, which are similar in catalytic activity to unsupported chromium oxide. The optimum results of KA-oil conversion and selectivity of 2,6-DMP were obtained for Cr(2.5 wt%)/MgO. The activities of magnesium oxide-supported chromium oxide catalysts are summarized in Table 4.

3.3. Influence of the reaction conditions

For the Cr(2.5 wt%)/MgO catalyst, the dependencies of KA-oil conversion and selectivity on reaction temperature are shown in Fig. 4. Both the conversion of KA-oil and the selectivities to 2,6-DMP and to 2,4,6-TMP increase, while to compensate that the selectivities to methylated cyclohexanol and methylated cyclohexanone decrease with reaction temperature. At 440°C and WHSV=0.4 h^{-1}, the formation rate of 2,6-DMP is 39 μmole/h g.

The KA-oil conversion and selectivity change as a function of space velocity are shown in Fig. 5. The formation rate of 2,6-DMP, attained 33 μmole/h g at 400°C, is more appreciable at lower space velocity. The selectivities to 2,6-DMP and to 2,4,6-TMP decrease, while to compensate that the selectivities to methylated cyclohexanol and methylated cyclohexanone increase with space velocity.

These results suggest that the methylated cyclohexanol and/or cyclohexanone are intermediates for the formation of methylated phenol (2,6-DMP and 2,4,6-TMP), while 2,6-DMP and 2,4,6-TMP are formed simultaneously from KA-oil and methanol in the reaction. The conclusion is strongly supported by a separate experiment, whose results are summarized in Table 5. 2,6-DMP was selectively formed in high yield from methanol and 1-methylcyclocyclohexanol as well as from methanol and 1-methylcyclohexanone.

Table 4
Summary of KA-oil reaction with WHSV=0.4 h^{-1} and methanol:KA-oil=10:1 at 1 atm and 400°C catalyzed by Cr/MgO catalysts

Catalyst	Reaction rate		Rate of 2,6-DMP formation	
	Catalyst (μmol/s g)	(μmol/s m^2)	Catalyst (μmol/s g)	(μmol/s m^2)
MgO	36.72	0.94	6.39	0.16
Cr(0.1 wt%)/Mg	57.61	1.28	24.50	0.54
Cr(2.5 wt%)/MgO	58.65	1.27	30.73	0.67
Cr(9 wt%)/MgO	56.39	1.28	24.20	0.55
Cr(10 wt%)/MgO	54.06	1.29	17.12	0.41
Cr(12 wt%)/MgO	57.50	1.25	19.03	0.41

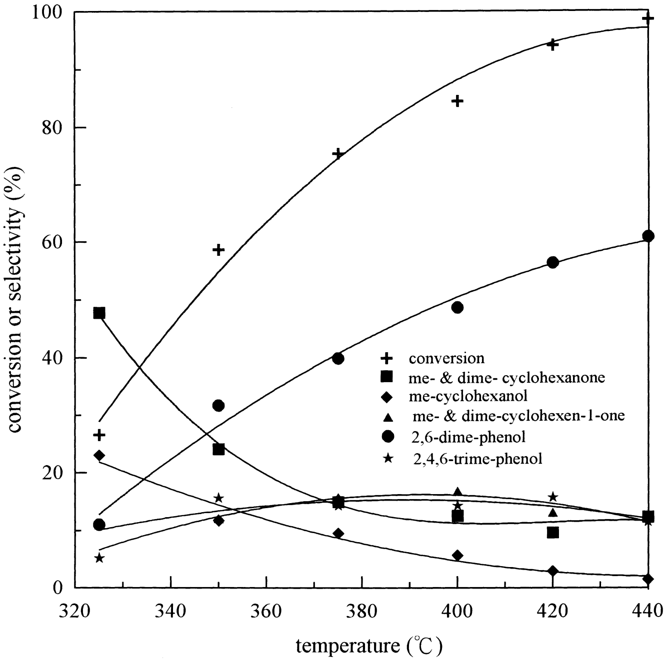

Fig. 4. Effect of reaction temperature on reaction of KA-oil and methanol at 1 atm, and methanol/KA-oil (mol)=10 over Cr(2.5 wt%)/MgO.

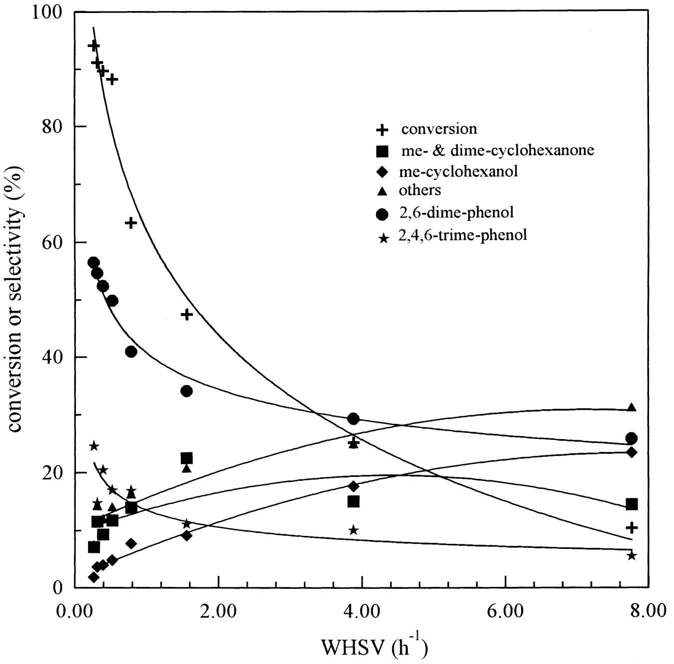

Fig. 5. Effect of space velocity on the reaction of KA-oil and methanol at 400°C, 1 atm, and methanol/KA-oil (mol)=10 over Cr(2.5 wt%)/MgO.

Table 5
Conversion and selectivity data for the various substrates reaction with WHSV=0.4 h^{-1} and methanol:substrate=10:1 at 1 atm and 400°C catalyzed by Cr(2.5 wt%)/MgO

Substrate	Conversion	Selectivity			
		me-Cyclohexanone	dime-Cyclohexanone	me- & dime-Cyclohexen-1-one	me-Cyclohexanol
me-Cyclohexanol	97.5	2.4	19.9	—	12.1
me-Cyclohexanone	85.7	—	39.7	8.6	19.8
2,6-DMP	9.8	—	39.2	—	42.1

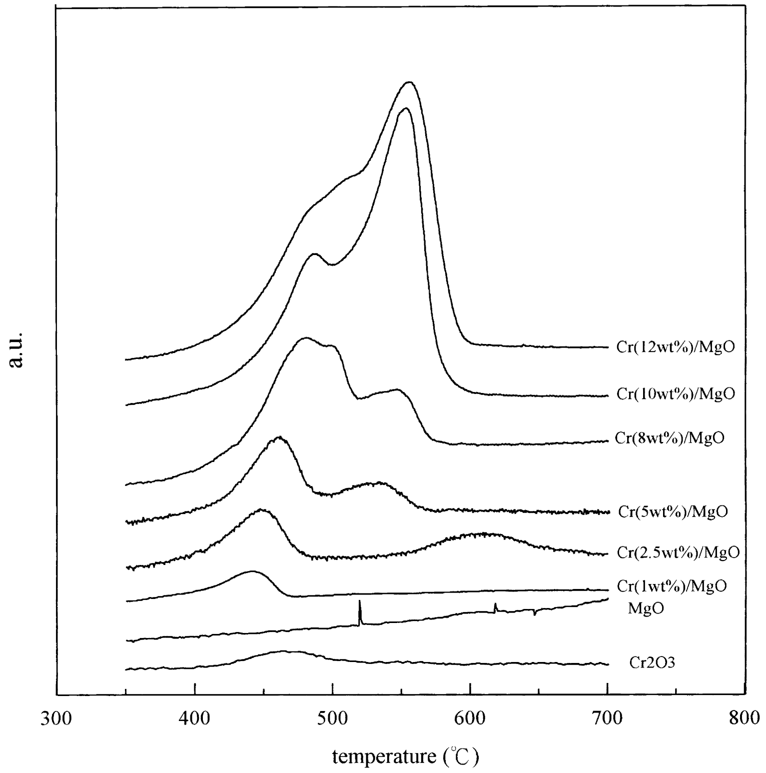

Fig. 6. TPR spectra (5% H_2) of Cr/MgO catalysts with different Cr content.

However, although 2,4,6-TMP was detected in the reaction of methanol and 2,6-DMP under these conditions, the yield of 2,4,6-TMP was very poor.

3.4. Temperature-programmed study

TPR spectra of various Cr/MgO catalysts are shown in Fig. 6. TPR spectrum of Cr_2O_3 shows a small reducing peak at 470°C, while that of the original MgO shows no peak. As Cr was loaded on MgO, the TPR spectra of these catalysts gave new peaks which were different from the spectra taken with Cr_2O_3 or MgO, especially for Cr(2.5 wt%)/MgO, which gives two reducing peaks at 450°C and 610°C, respectively. These two peaks shift and come closer as the content of Cr in Cr/MgO increases. It seems reasonable to assume, therefore, that Cr and MgO interact on the MgO surface. In addition, no particles of Cr_2O_3 can be

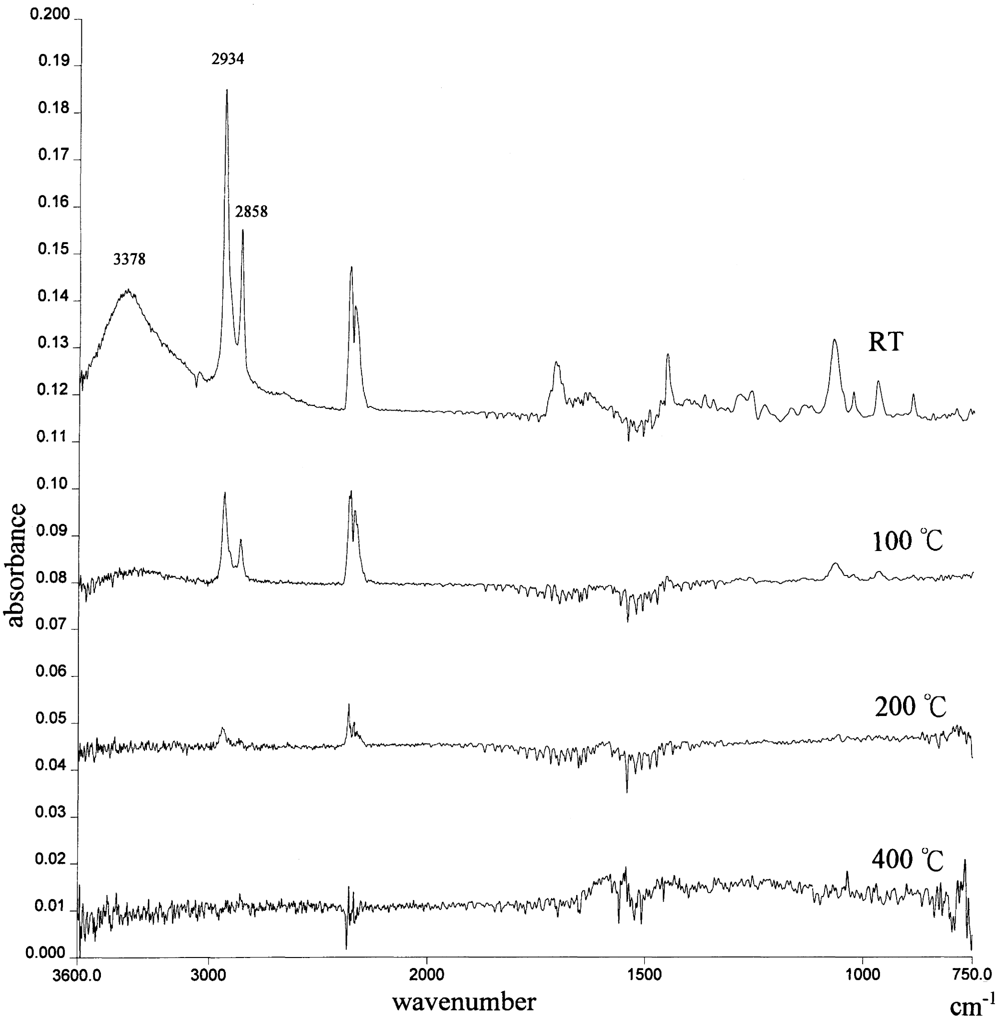

Fig. 7. Infrared spectra of cyclohexanol adsorbed on the Cr(2.5 wt%)/MgO catalyst as a function of evacuation temperture.

found by XRD measurement from Cr/MgO, but the catalysts have a color similar to Cr_2O_3 (Fig. 1). These results suggest that Cr exists as fine chromium oxide particle, which is an essential constituent for the reaction.

3.5. FTIR measurements

Figs. 7 and 8 show that IR spectra measured after adsorption of 10 Torr cyclohexanol and cyclohexanone on Cr(2.5 wt%)/MgO at 20°C, respectively, followed by evacuation at successively higher temperature up to 400°C. As seen in Fig. 7, at 20°C, there is a pair of broad absorption bands 1659 and 3378 cm^{-1}, which correspond, respectively, to stretching and bending modes of the OH group in cyclohexanol. The bands mostly diminish rapidly in intensity as temperature is elevated and disappear at 100°C. On the contrary, instead of cyclohexanol, when cyclohexanone is used for adsorption, a 1719 cm^{-1} absorption band appears corresponding to the carbonyl group of cyclohexanone. Although the intensity of the 1719 cm^{-1} absorption band decreases with temperature, it still exists even at 200°C (Fig. 8). This suggests that cyclohexanone is strongly adsorbed than

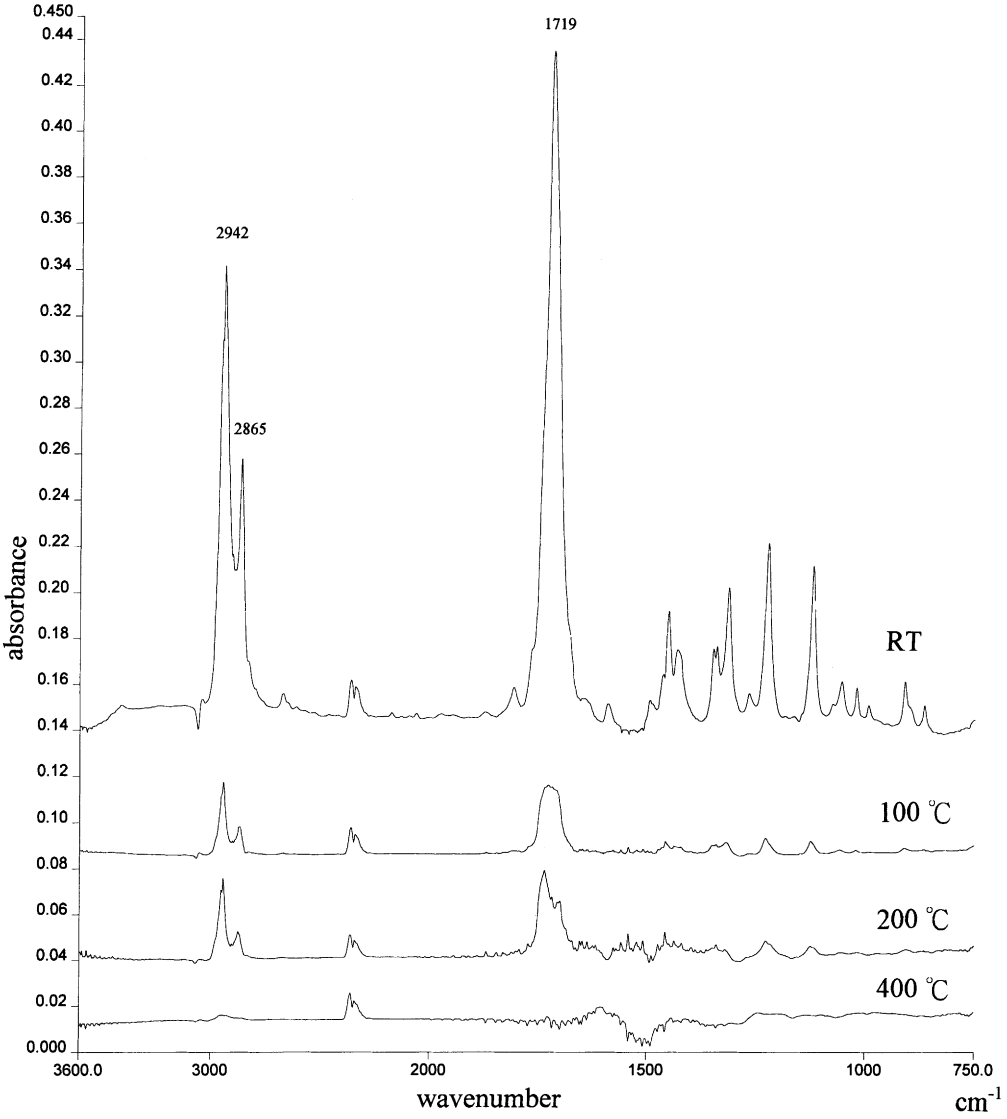

Fig. 8. Infrared spectra of cyclohexanone adsorbed on the Cr(2.5 wt%)/MgO catalyst as a function of evacuation temperature.

cyclohexanol on the surface. Fig. 9 shows IR spectra measured after exposure to a mixture of hydrogen (100 Torr) and cyclohexanone vapor (10 Torr) at 20°C followed by elevation of the temperature without evacuation. At 20°C, the spectrum shows only one band at 1717 cm^{-1}, indicative of the existence of a carbonyl group. At higher temperature the carbonyl band disappears, which is different from the results illustrated in Fig. 8. When the catalyst was cooled down to 20°C, the absorption of 1717 cm^{-1} appears again with a new absorption band at 3238 cm^{-1} which may be due to OH groups as described in Fig. 8. This indicates that cyclohexanol and cyclohexanone co-exist as in the gas phase and cyclohexanol is produced from the reaction of cyclohexanone with hydrogen. These results show again the specialty of Cr/MgO which maintain the OH group through the reaction indicated previously.

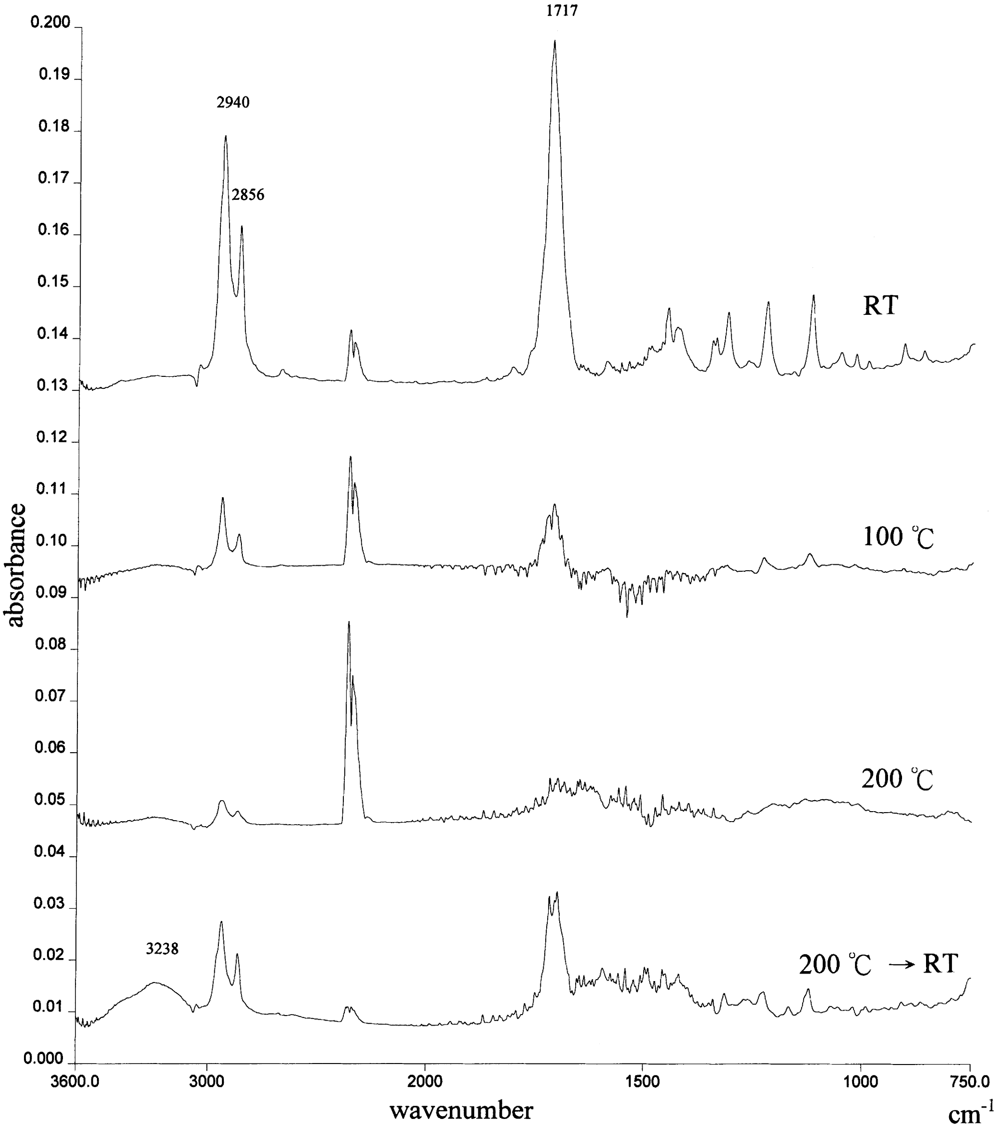

Fig. 9. Infrared spectra of cyclohexanone and hydrogen adsorbed on the Cr(2.5 wt%)/MgO catalyst as a function of catalyst temperature without evacuation.

4. Conclusions

Catalytic synthesis of 2,6-dimethylphenol from methanol and KA-oil was achieved in a step by using magnesium oxide-supported chromium oxide catalysts. The catalytic properties of magnesium oxide can be enhanced only by addition of a fairly small amount of chromium. At high conversion (>90%), dimethylphenol was formed in high yield (>60%) with minor amounts of methylated cyclohexanol and/or cyclohexanone, which may further be reacted to form the desired product. FTIR experiments indicated that cyclohexanol adsorbed on the Cr/MgO surface was weak than cyclohexanone, and that cyclohexanone converted to cyclohexanol in the presence of hydrogen at higher temperature over Cr/MgO catalysts.

Acknowledgements

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