Vapour Phase Alkylation of Naphthalene over Lanthana Modified Zeolites

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Abstract: Lanthanum oxide impregnated large-pore zeolite catalysts were prepared. The catalysts were characterized by XRD (X-ray diffraction), PSA (particle size analysis), TPD (temperature programmed desorption) and SEM (scanning electron microscope). The performances of the catalysts were investigated using the alkylation reaction of naphthalene with methanol. Under comparable conditions, the La-impregnated β-zeolite catalyst showed the highest catalytic activity among all the catalysts tested. The lower reaction temperature is favorable for the formation of 2,6-dimethyl naphthalene.

Key words: Naphthalene, methanol, 2,6-dimethyl naphthalene, alkylation, zeolite.

1. Introduction

The polycyclic aromatic hydrocarbons (namely naphthalene) present in coal derived liquids and heavy oils can be utilized for making value added chemicals. There is growing interest in recent years to convert naphthalene to produce 2-alkyl naphthalene and 2,6-DANs (2,6-dialkyl naphthalenes). 2,6-DAN can be oxidized and esterified to give dimethyl 2,6-NDC (2,6-naphthalene dicarboxylate). This monomer undergoes polycondensation with ethylene glycol to give PEN (polyethylene naphthalate). 2-MN (2-methylnaphthalene) is the main raw material in vitamin K synthesis and 2,6-DMN (2,6-dimethylnaphthalene) is used in the preparation of polyester fibers and plastics with improved mechanical, thermal and gas barrier properties compared with that of PET (poly ethylene terephthalate) [1].

The only commercial process is that by the BP-Amoco company for producing 2,6-DMN, which requires four successive reaction steps starting from o-xylene and butadiene that uses a HF_3-BF_3 based

catalyst [2]. This process brings forth an additional problem of the catalyst disposal. Because of the multistep processing involved in obtaining 2,6-DMN, and further processing to NDC and PEN, the PEN polymer is presently priced at a significant premium to PET. An alternative to this problem may be the exploration of the possible use of zeolites as catalyst in the alkylation of naphthalene. An additional advantage is that zeolites are environmentally benign and are easier to handle.

Alkylating agents such as methyl alcohol [3-5], ethyl alcohol [6], isopropyl alcohol [7-10], propylene [11-13], isopropyl bromide [14] and tertiary butyl alcohol [1, 9, 15] have been applied successfully to the selective formation of 2,6-dialkyl naphthalene. Among the various 2,6-DAN, 2,6-DMN is preferred, because no carbon atoms are lost during its oxidation to NDC, a necessary step in the manufacture of PEN. Moreover, it results in a high yield and corresponds well to the atomic economy. Therefore, an efficient catalyst that operates under mild conditions is highly desirable to realize the practical production of 2,6-DMN via naphthalene methylation. Recently, a variety of zeolites, mainly ZSM-5, ZSM-11, MCM-22, zeolite β and mordenite, have been utilized as catalysts

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in the naphthalene methylation reaction [16-19]. Wen et al. [20] used HZSM-5, Hβ, HUSY and SAPO-11 as catalysts for the synthesis of 2,6-DMN and SAPO-11 showed high selectivity for 2,6-DMN. But the stability was very poor and most of the activity lost after 4 h of reaction.

In this paper, we have modified the zeolites with La_2O_3 to improve the selectivity and stability of the catalysts for the synthesis of 2,6-DMN. In this work, the methylation of naphthalene with methanol as the alkylating reagent was investigated using a gas phase fixed bed reactor over La_2O_3 (lanthana) modified large-pore zeolites, such as β-zeolite, mordenite and zeolite L. Catalytic performances are discussed in relation with physicochemical properties of catalysts.

2. Experiments

2.1 Catalyst Preparation

All chemicals used were of analytical grade. Zeolites were obtained from Zeochem A G, Switzerland. It was modified using metal nitrate salt by wet impregnation method. In a 500 mL beaker, required amount of lanthanum nitrate salt was taken and 150 mL of distilled water was added and stirred to get uniform solution. To this solution, 20 g of zeolite was added and stirred thoroughly at 30 °C for 3 h. Then, the catalyst was dried in an air oven and calcined at 450 °C for 4 h. Some of the physico-chemical properties of zeolites used are presented in Table 1.

2.2 Methylation of Naphthalene

Alkylation of naphthalene was carried out in a continuous flow pyrex glass reactor with 20 mm id (internal diameter) and length 30 cm under atmospheric pressure, using 10 g catalyst (6-14 mesh size). The reaction mixture of naphthalene and methanol (1:6 molar ratio) with mesitylene as solvent was fed into the reactor using a peristaltic syringe pump. The product was condensed and collected at the bottom and analysed by GC (gas chromatography) using BPX 50 capillary column of 30 m length fitted to FID (flame ionisation detector).

2.3 Catalyst Characterization

The X-ray diffractograms were recorded in D-8 ADVANCE diffractometer (Bruker AXS, Germany) using CuKα radiation at 40 kV and 40 mA in parallel beam geometry. SEM (scanning electron microscopy) images were recorded using the ZEISS EVO 50 scanning electron microscope.

3. Results and Discussion

Naphthalene alkylation is an interesting and complicated reaction system. Naphthalene has two aromatic rings, strongly reducing directing electronic effects. The α-position is considered to be kinetically favored, whereas the β-position is thermodynamically favoured. The dialkyl naphthalenes are prone to many types of reactions such as isomerization, transalkylation and dealkylation [21, 22]. Selective dimethylation of naphthalene to 2,6-DMN is an important step towards an attractive route to 2,6-naphthalene dicarboxylic acid. To achieve this, molecular shape-selectivity has been proposed to discriminate among the dialkyl naphthalene isomers based on their molecular dimensions.

The reaction of naphthalene with methanol was studied at 300 °C, naphthalene-methanol mole ratio of 6 and WHSV (weight hourly space velocity) 1.5, using mesitylene as solvent. GC analysis revealed the formation of 2-MN, 1-MN and 2,6-DMN as major

Table 1   Some physico-chemical properties of zeolites.

Sample No.	Properties	β-Zeolite	Mordenite	Zeolite (L)
1	SiO_2/Al_2O_3 molar ratio	27	25	5.9
2	Surface area (BET) (m^2)	700	500	220
3	Pore size (Å)	7.6 × 6.4	6.5 × 7.0	7.1
4	Crystal size (SEM) (μm)	0.2 × 0.4	< 1	1-2

products. The other dialkyl-naphthalenes and polyalkyl-naphthalenes were shown as others. Analysis of the products also indicated that alkylation took place preferentially at 2- and 6-positions of naphthalene. It was also observed that 2-MN was formed predominantly compared to 1-MN.

Alkylation of naphthalene with methanol over different zeolites is presented in Table 2. The conversion of naphthalene increases in the order of the zeolite L < mordenite < zeolite-β. The conversions of naphthalene for zeolite L and mordenite at the reaction temperature 300 $^{\circ}$C are 37.2% and 38.4%, respectively. The naphthalene conversion of zeolite-β is 40.3% at 300 $^{\circ}$C.

The authors have studied the naphthalene methylation reaction on three kinds of La$_2$O$_3$ modified zeolites, e.g., β-zeolite, mordenite and zeolite L. The catalytic performances of these samples are listed in Table 3. These results showed that a shape-selective effect had strongly taken place on methylation of naphthalene over the zeolite catalysts. The 2,6-DMN selectivity of these modified zeolites increases in the

sequence of La$_2$O$_3$-mordenite < La$_2$O$_3$-zeolite L < La$_2$O$_3$-zeolite-β. La$_2$O$_3$-zeolite-β showed a selectivity of 18.4% 2,6-DMN, which is higher than the selectivities of other two catalysts under same conditions.

Table 4 shows the alkylation of naphthalene with methanol over different La$_2$O$_3$ supported β-zeolite catalysts. La$_2$O$_3$ were prepared from different source materials and impregnated over zeolite β. The catalytic performances of these catalysts as presented in Table 4 show that La$_2$O$_3$ (prepared from La(NO$_3$)$_3$·6H$_2$O) supported on β-zeolite showed better conversion (52.3%) as well as better selectivity (18.4%) for 2,6-DMN than other La$_2$O$_3$ supported β-zeolite catalysts.

Fig. 1 presents the effect of different reaction temperatures on naphthalene conversion and product selectivity for methylation of naphthalene over La$_2$O$_3$-β-zeolite catalyst. As shown in Fig. 1, the conversion of naphthalene over the catalyst increased with the increase in temperature from 250 $^{\circ}$C to 300 $^{\circ}$C, which may be attributed to the domination of the

Table 2   Alkylation of naphthalene with methanol over different zeolites.

Sample No.	Catalyst	Conversion (%)	Product selectivity (%)			
			2-MN	1-MN	2,6-DMN	Others
1	Zeolite β	40.3	43.1	32.5	12.1	12.3
2	Mordenite	38.4	42.8	32.6	11.4	13.2
3	Zeolite L	37.2	42.3	32.1	11.9	13.7

Table 3   Alkylation of naphthalene with methanol over La$_2$O$_3$ supported on different zeolites.

Sample No.	Catalyst	Conversion (%)	Product selectivity (%)			
			2-MN	1-MN	2,6-DMN	Others
4	La$_2$O$_3$-zeolite β	52.3	42.8	33.2	18.4	5.6
5	La$_2$O$_3$-mordenite	50.6	44.3	32.7	16.1	6.9
6	La$_2$O$_3$-zeolite L	48.7	46.3	30.7	17.2	5.8

Table 4   Alkylation of naphthalene with methanol over different La$_2$O$_3$ supported β-zeolite.

Sample No.	Catalyst	Conversion (%)	Product selectivity (%)			
			2-MN	1-MN	2,6-DMN	Others
1	A	44.5	41.4	35.3	17.2	6.1
2	B	46.2	42.3	36.6	15.2	5.9
3	C	50.7	43.5	33.5	16.8	6.2
4	D	52.3	42.8	33.2	18.4	5.6

A—commercial La$_2$O$_3$, B—La$_2$O$_3$ from LaCl$_3$·7H$_2$O, C—La$_2$O$_3$ from La$_2$(CO$_3$)$_3$, D—La$_2$O$_3$ from La(NO$_3$)$_3$·6H$_2$O.

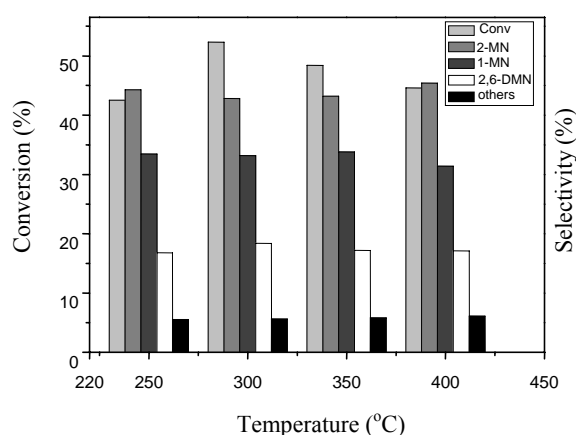**Fig. 1 Effect of temperature on the alkylation of naphthalene with methanol.**

Fig. 2 Effect of duration of the run on the alkylation of naphthalene with methanol.

alkylation at lower temperature upto 300 °C. Beyond this temperature, the conversion of naphthalene decreased from 52.3% to 44.6% as the temperature was raised to 400 °C. This behavior may be due to the fact that the speed of dealkylation reaction is faster than that of alkylation reaction at the higher temperature.

Effect of duration of the run on the alkylation of naphthalene with methanol: A series of experiments were conducted using La_2O_3-β-zeolite in which the duration of the reaction was varied from 1 h to 10 h. The catalyst was regenerated after each experiment by passing air at 475 °C for 4 h. Fig. 2 illustrates the results of catalytic activity with time on stream. The conversion values for naphthalene methylation are almost unaltered till 10 h of time on stream. This confirms that the deactivation of the catalyst is essentially due to external coking originated by cracking of feed materials.

The catalysts were characterized by XRD (X-ray diffraction), PSA (particle size analysis), TPD (temperature programmed desorption) and SEM (scanning electron microscope). XRD patterns of catalysts are presented in Fig. 3. XRD showed interaction among the active oxides and the support. The XRD studies revealed that crystalline structure is retained even after lanthanum oxide modification of the zeolites.
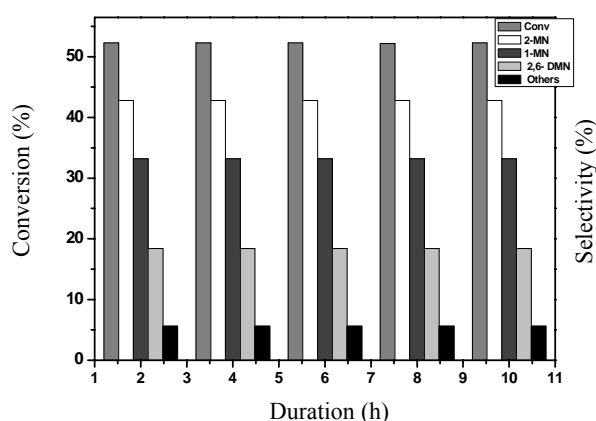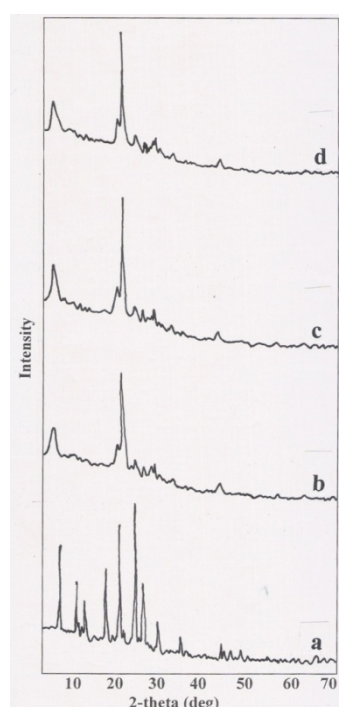

Fig. 3 XRD of (a) La_2O_3-β-zeolite; (b) La_2O_3-mordenite; (c) La_2O_3-zeolite L and (d) β-zeolite catalysts.

Particle size distribution profiles of the catalysts as shown in Table 5 are excellent. Span, a measure of the width of a distribution, is calculated using Eq. (1):

$$(D_{90} - D_{10})/D_{50} \qquad (1)$$

where, D_{90} = 90% of the particle are below this diameter, D_{50} = 50% of the particle are below this diameter and D_{10} = 10% of the particle are below this diameter, which is small for all the samples. A small span indicates uniform distribution, since it reflects distribution from mid-point (D_{50}).

Table 5   Particle size profile of the catalysts.

| Sample No.	Catalyst	D_{90} (μm)	D_{50} (μm)	D_{10} (μm)	$D_{90\text{-}50}$ (μm)	$D_{50\text{-}10}$ (μm)	Span
1	La_2O_3-β zeolite	1.23	0.72	0.29	0.51	0.43	1.31
2	La_2O_3-mordenite	1.81	1.00	0.38	0.81	0.62	1.43
3	La_2O_3-zeolite L	1.76	0.98	0.31	0.78	0.67	1.48
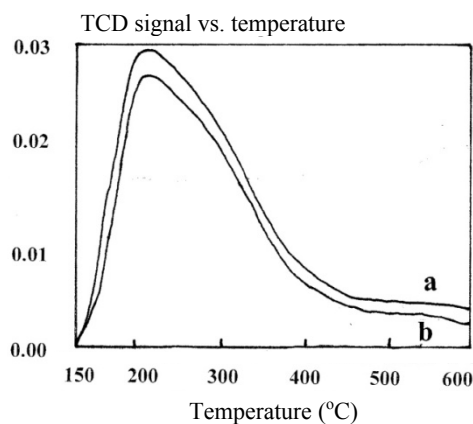
Fig. 4   TPD profile of (a) β-zeolite and (b) La_2O_3-β-zeolite catalyst.

Fig. 4 shows the TPD profiles of two catalyst samples. It can be seen that β-zeolite exhibits strong acid strength. The acid strength of the La_2O_3-modified β-zeolite has decreased. The conversion of naphthalene to methyl naphthalenes for La_2O_3-modified β-zeolite catalyst is higher than that of β-zeolite. This showed that an optimum acidity on the catalyst is needed for better conversion of naphthalene.

Representative SEM images obtained for La_2O_3-β-zeolite, La_2O_3-mordenite, La_2O_3-zeolite L and zeolite-β catalysts are shown in Fig. 5. The SEM image of β-zeolite suggests that the material has well defined agglomerated morphology corresponding to crystalline structure. On loading the La_2O_3 over the zeolite, it is observed that the material is well dispersed over the support. Thus, the conversion of the desired compound was found to increase from 40.3% to about 52.3% using modified β-zeolite catalyst.

(a)

(b)

(c)

(d)
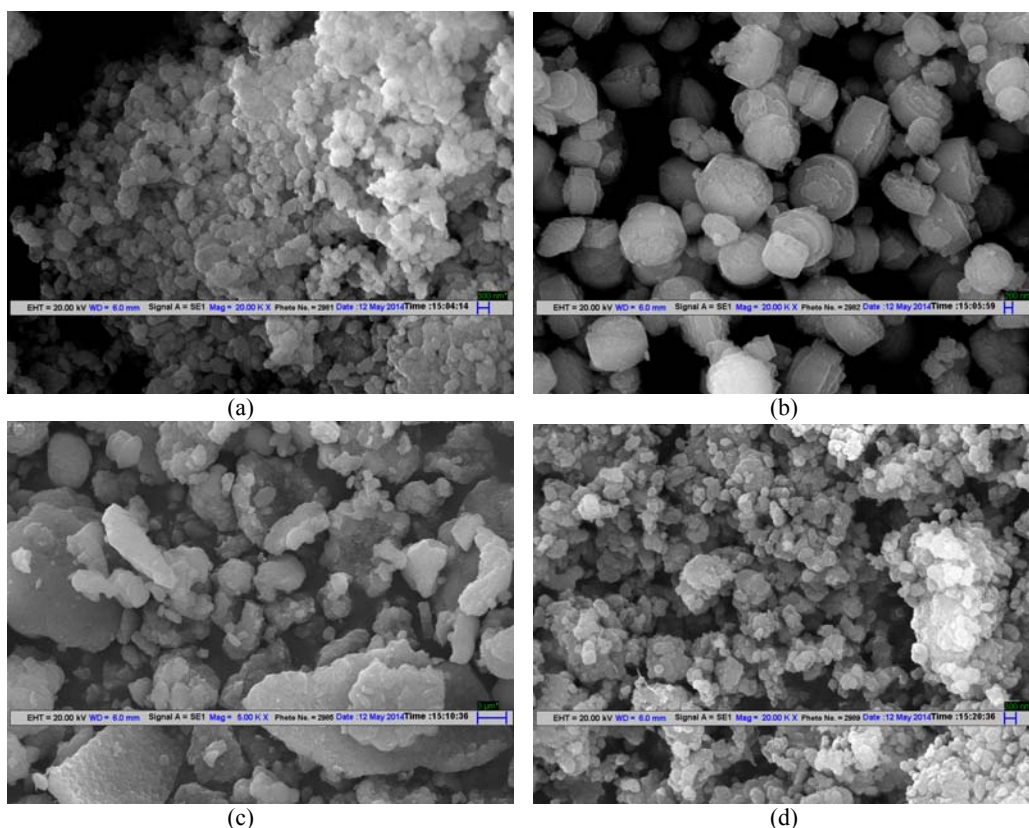
Fig. 5   SEM images of (a) La_2O_3-β-zeolite, (b) La_2O_3-mordenite, (c) La_2O_3-zeolite-L and (d) β-zeolite catalysts.

4. Conclusions

The lanthanum oxide impregnated large-pore zeolite catalyst exhibited excellent catalytic activity for methylation of naphthalene. Among the catalysts tested, La_2O_3 impregnated β-zeolite showed the highest conversion (52.3%) of naphthalene. XRD studies give complete information of active phases which are responsible for better activity and selectivity of the catalyst towards the formation of methyl naphthalenes and dimethyl naphthalenes. The high performance of the catalyst may be attributed to the combined effect of physico-chemical properties of the support and the catalyst. The reusability test exhibits the good recycling capacity of the La_2O_3 impregnated β-zeolite catalyst.

Acknowledgments

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