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Selective aromatization of biomass derived diisobutylene to *p*-xylene over supported non-noble metal catalysts

Gangli Zhu, Pinhong Li, Feng Zhao, Huanling Song*, Chungu Xia*

State Key Laboratory for Oxo Synthesis and Selective Oxidation, Suzhou Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou 730000, China

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ABSTRACT

To obtain the valuable *p*-xylene from biomass with a high selectivity, several transition non-noble metals as main components of catalysts for aromatization of diisobutylene were explored. A volcano curve with the top marked by Cr(3d⁵4s¹) could be found between the activity and the atomic outer-shell electrons number of transition metals. The further addition of alkaline earth metal showed that the modification of surface properties by Mg doping could improve the catalytic performance. With Cr–Mg–Al–O as catalysts, the enhanced selectivity and single pass yield for the *p*-xylene formation could be obtained. Meanwhile, the side reaction of cracking could be suppressed, which might be attributed to the increment of the weak/strong acid ratio by Mg addition. Moreover, the catalysts kept a stable catalytic performance in the regeneration and reuse cycles.

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1. Introduction

p-Xylene (PX) is an important organic compound, mainly as raw material for production of polyester terephthalate (PET), widely used in textiles, coatings and electronics. Conventional *p*-xylene production technologies relied on the disproportionation and transalkylation, xylene isomerization process. Some other new processes are also being developed for production of aromatics such as aromatization from methane [1–3], ethane [4], propane [5], isobutane [6], olefin [7], methanol [8,9], glycerol [10], light alkanes [11] and heavier *n*-paraffins [12]. Most of these technologies, however, are strongly dependent on fossil resources. It is important to obtain fuels and basic chemicals from other resources like the biomass.

A number of researches explored the biomass route to produce xylenes. The direct catalytic pyrolysis of biomass was investigated. Using an integrated catalytic approach, biomass derived oils [13,14] can be converted into industrial commodity chemical feedstocks including xylenes. However, the mixture of C₈ aromatics isomers (such as *o*-xylene, *m*-xylene, *p*-xylene and ethylbenzene) with similar physical and chemical properties could be produced at the same time. The indirect route which utilizes biomass derivatives to produce aromatics is the other choice. Diels–Alder cycloaddition

with furans and ethylene and subsequent dehydrative aromatization are potentially valuable processes for sustainable conversion of biomass-derived furans to aromatics [15,16]. This route could selectively yield *p*-xylene. A similar idea is the cycloaddition of biobased acrylic acid and biobased isoprene to produce terephthalic acid [17]. Its challenge is the polymerization of olefins catalyzed by acid catalysts which is also required to improve para-selectivity in the cycloaddition. The indirect routes that start from biomass derived alcohols are also being researched. Huang et al. [18] attempted to transform isobutyl alcohol to aromatics over zeolite-based catalysts. The products were a mixture of toluene, xylenes and alkanes. It provided a promising alternative of direct pyrolysis of biomass, because the isobutyl alcohol could be obtained from biomass resources [19–22]. Another process [23] did not apply isobutyl alcohol as raw material to produce aromatics immediately, but firstly experienced the dehydration of isobutyl alcohol to isobutylene, and then followed by oligomerization and dehydrocyclization to yield aromatics. Wang et al. [24] declared a method of directly converting bio-ethanol to isobutylene, with the yield of about 83% in the optimized conditions. With increased availability and reduced cost, isobutylene or diisobutylene derived from bio-ethanol and isobutanol, can then be viewed as important platform molecules for biomass-to-PX transformation.

One of the challenges in the biomass-to-PX route is the aromatization of diisobutylene into *p*-xylene, which aims to improve the selectivity to *p*-xylene and avoid the cracking of the reactant as

* Corresponding authors.

E-mail addresses: songhl@licp.cas.cn (H. Song), cgxia@licp.cas.cn (C. Xia).

much as possible owing to the reaction under high temperature (around 500 °C).

In this work, we explored several transition non-noble metals as main components for selective aromatization. The effect of addition of alkaline earth metals was examined. Moreover, the surface properties modified by Mg doping were discussed. The performance of catalysts in regeneration and reuse cycles was further investigated for potential application.

2. Experimental

2.1. Catalyst preparation

The M/Al₂O₃ Catalysts were prepared by impregnation method using pelletized γ -alumina balls (diameter 1.5–1.7 mm) as support. After calcined at 600 °C for 4 h, the γ -alumina balls were respectively impregnated with salts solution (Cr(NO₃)₃, Fe(NO₃)₃, Co(NO₃)₂, Ni(NO₃)₂, Zn(NO₃)₂, NH₄VO₃, (NH₄)₂Mo₂O₇, analytical grade pure) under continuous stirring for 10 h, and then again dried and calcined at 600 °C for 4 h. The metal loading amount was 5% (mass fraction) in the M/Al₂O₃ catalysts. The Cr–Al–O catalysts were prepared in the same way with the loading amount from 1% to 20% (calculated based on Cr mass fraction). For example, to prepare 5% Cr/Al₂O₃ catalyst, 40 g Al₂O₃ was added to a solution prepared with 16.2 g Cr(NO₃)₃·9H₂O and DI-water. The Cr–AE–Al–O catalysts (denoted as CrAE) were prepared by stepwise impregnation method. The alumina balls were first treated with solution of alkali earth salts (Mg(NO₃)₂, Ca(NO₃)₂, Ba(NO₃)₂, analytical grade pure), dried and calcined at 600 °C. And then, 5% Cr was loaded in the same way as that of M/Al₂O₃ preparation. The Cr–Mg–Al–O catalysts were prepared in a similar procedure with the Mg loading amount (calculated based on MgO mass fraction) from 0.75% to 3%. The catalyst with *x*% Mg loading was denoted as CrMgx.

2.2. Catalytic reaction

The reaction was conducted in a fixed bed catalytic reaction apparatus. Catalysts were loaded in a stainless steel reactor (18 mm i.d., 500 mm in length). Diisobutylene (77.5% 2,4,4-tris-methyl-1-pentene, 22.5% 2,4,4-trimethyl-2-pentene) was used as the raw material and pumped into the reactor with a preheater. The N₂ diluent gas was introduced in and mixed with diisobutylene in the preheater. The gas flowrate was controlled by a mass flow controller. The reaction temperature was set at 450–550 °C and pressure was maintained at 0.1 MPa. Diisobutylene was fed into catalyst bed and the reaction occurred when the desired reaction condition was achieved. After reaction, the products were separated into gaseous products and liquid products in a condenser. The liquid products were collected every 5 min in a sealed glass vial, and analyzed by gas chromatogram equipped with FID detector and 0.25 × 30 m capillary column. The gaseous products were analyzed by an online gas chromatogram equipped with a TCD detector and Hayesep D packed column. The composition of products was analyzed by GC–MS (Agilent 6890A-5975C). The main side reactions were cracking, hydrogenation and coking. The cracking reaction mainly produced gas compounds including one to four carbon hydrocarbons, in which C₄ was predominant (92%), with a little amount of C₁(1%), C₂(3%) and C₃(4%) hydrocarbons. In the liquid phase, the isooctane produced by hydrogenation was the main by product. In the solid phase, the coking type was possibly aliphatic cokes. The carbon balance was calculated and the difference of carbon flow between influents and effluents was less than 5%. In the regeneration and reuse cycles, the coke was burned off in an air flow at about 500 °C and purged with N₂ flow before each cycle (Scheme 1).

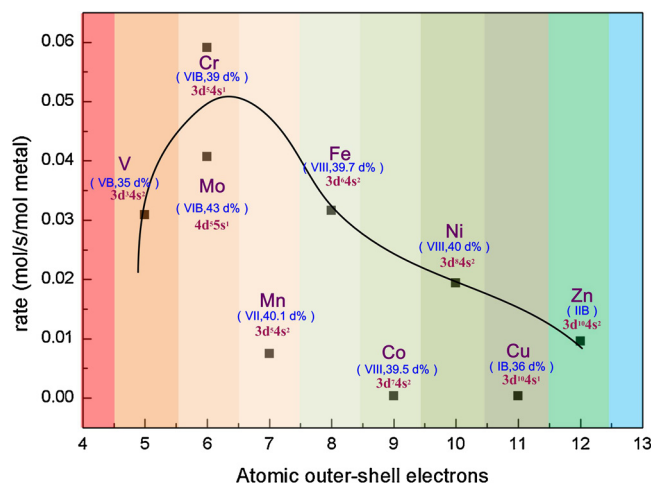


Fig. 1. Activity of some transition non-noble metal for aromatization.

Rate of *p*-xylene formation (y axis) plotted against atomic outer-shell electrons (x axis); *d*%: *d*-character factor; test conditions: pressure 0.1 MPa, 520 °C, feedstock/N₂ = 1:1, WHSV = 1 h⁻¹.

2.3. Characterization of catalysts

The specific surface area and pore size distribution of catalysts were analyzed by surface area and porosity system (Micromeritics Tristar II 3020). The sample was degassed at 300 °C for 3 h. The phase composition analysis was done in a XRD system (Bruker D8 Discover X) with Cu-K α radiation ($\lambda = 0.1541$ nm). H₂-TPR test was conducted in a U-shaped quartz tube. The sample firstly was loaded and pretreated in a N₂ flow at 200 °C for 3 h and cooled to the room temperature, and then raised to 750 °C at a ramp of 10 °C/min in a 5% H₂/N₂ mixture gas. The acid sites distribution of catalysts was studied by NH₃-TPD. Typically, 100 mg catalyst was pretreated at 400 °C for 1 h under He atmosphere and cooled down to 100 °C. Then, 10% NH₃/He was adsorbed until saturated, and subsequently the sample was swept by a flowing purge gas of He stream at 100 °C. Finally, the sample was heated at a rate of 10 °C/min in a flowing He and the desorption curve was recorded. Sample loop was used to pulse inject 440 μ L 10% NH₃/He and the corresponding response was recorded for calibration. Catalysts were also characterized by Lambda 650S UV–vis spectrometer (PerkinElmer). Sample powder was well ground with BaSO₄ prior to the measurement. The coking was analyzed by the thermal analysis instrument (Mettler TGA/DSC-1), FTIR (Nicolet Nexus 870) and elemental analyzer (Vario EL CHNOS).

3. Results and discussion

3.1. Activity of some transition non-noble metals

To find the possible effective catalyst for aromatization, some supported transition non-noble metal catalysts were tested in a fixed bed reactor, and the results are shown in Fig. 1. It seems there is a volcano curve when the activity (of *p*-xylene formation) is correlated with atomic outer-shell electrons. Both Cr(3d⁵4s¹) and Mo(4d⁵5s¹) in group(VI B), had achieved the better activity than the others. The lattice energy, cohesive energy and enthalpy of sublimation usually have the similar volcano curves [25,26], whose summits are also at around group(VI B) with six atomic outer-shell electrons. The reasons of volcano curve relation of atomic outer-shell electrons and aromatization activity are still obscure. The *d* character % [27–29], which has close relation with adsorption/desorption, is deemed as important guidelines for the catalyst design. For example, metals with *d* character % of 40–50 *d*% might

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