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Esterification of Acetic Acid with *n*-Butanol Using Molybdenum Oxides Supported on γ-Alumina

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Abstract Two γ-alumina-supported molybdenum oxide catalysts with different Mo loadings were prepared by the impregnation of a precipitated alumina. The alumina support and the supported catalysts were characterized using X-ray diffraction, N_2 adsorption and NH_3-TPD techniques and tested in the liquid-phase esterification of acetic acid with *n*-butanol. The effects of the reaction time, of the molar ratio of the reactants, of the speed of agitation and of the mass fraction of the catalyst on the catalytic properties were studied. After only 120 min of reaction at 100 °C with an *n*-butanol to acetic acid mole ratio equal to 3 the conversion reached 81% in the presence of the supported catalyst containing 10 wt% MoO_3 (10Mo–Al_2O_3 sample). The conversion as well as the total NH_3-TPD acidity increased in the following order: $Al_2O_3 < 5Mo-Al_2O_3$ (5 wt% MoO_3/Al_2O_3) < 10Mo–Al_2O_3. The selectivity of *n*-butyl acetate was, in all cases, 100%. No loss in catalytic activity and product selectivity after three cycles with 10Mo–Al_2O_3 catalyst was observed.

Keywords Esterification · Acetic acid · *n*-Butanol · Butyl acetate · γ-Alumina-supported molybdenum oxide

1 Introduction

Esters are most commonly prepared by direct esterification of carboxylic acids with alcohols in the presence of acid catalysts [1]. Both homogeneous and heterogeneous catalysts have been used to accelerate the esterification reactions. While the mineral acids, such as H_2SO_4, HCl, HF, $ClSO_2OH$, can be given as examples of the homogenous catalysts [2], cation-exchange resins [3, 4], zeolites [5, 6] or supported heteropolyacids [2, 7–9] could serve as heterogeneous catalysts.

Even though the homogeneous acid catalysts are widely used at industrial scale for their low price, they are toxic, corrosive and often hard to be recovered from the reaction solution. On the other hand, the solid catalysts have some advantages: they can be separated from liquid reaction mixture by filtration or decantation, have high selectivity and, last but not least, they are environmentally friendly. Therefore, the replacement of the homogeneous acid catalysts by solid acid catalysts is a challenge of heterogeneous catalysis. To our knowledge, there are no studies investigating alumina-supported molybdenum oxides as catalysts for the esterification of *n*-butanol with acetic acid. Butyl acetate, as the most of alkyl acetates, is generally used as solvent, as component in flavoring and as additive in perfumes [1].

In the present study, the esterification of *n*-butanol with acetic acid, without adding a catalyst and heterogeneously catalyzed with alumina and alumina-supported molybdenum oxides, has been studied. The effects of the reaction time, the molar ratio between the reactants, the speed of

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agitation and the catalyst loading on the reaction were investigated.

2 Experimental

2.1 Catalyst Preparation and Characterization

Al_2O_3 support was prepared from $Al(NO_3)_3 \cdot 9H_2O$ (Fluka Analytical) by precipitation with ammonium carbonate (Lachema) at controlled pH of 6.5. MoO_3 was introduced at two concentrations, 5% and 10% by weight, via incipient wetness impregnation of the alumina support with aqueous $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Fluka Analytical) solutions containing appropriate amounts of molybdenum. After impregnation, the samples were dried in air at 100 °C and then calcined at 600 °C for 4 h. The 5 wt% MoO_3/Al_2O_3 and 10 wt% MoO_3/Al_2O_3 samples were labelled 5Mo–Al_2O_3 and 10Mo–Al_2O_3, respectively.

The crystalline phases were investigated by the X-ray diffraction (XRD) method. XRD patterns were obtained with a Philips PW 3710 type diffractometer equipped with a CuK_α source ($\lambda = 1.54$ Å), operating at 50 kV and 40 mA. They were recorded over the 10–70° angular range with 0.02° (2θ) steps and an acquisition time of 1 s per point. Data collection and evaluation were performed with PC-APD 3.6 and PC-Identify 1.0 software.

Surface areas of the catalysts were measured from the adsorption isotherms of nitrogen at 77 K using the BET method with a Micromeritics ASAP 2020 sorptometer.

The acidity of the catalysts was estimated by temperature-programmed desorption of ammonia (NH_3-TPD). About 0.1 g of the catalyst sample was dehydrated at 500 °C in dry air for 1 h and purged with N_2 for 0.5 h. The sample was then cooled down to 100 °C under the flow of N_2, and NH_3 was supplied to the sample until its saturation. For the desorption of the physisorbed ammonia, a nitrogen stream was passed over the sample, at the same temperature, until no more NH_3 was observed in the exit flow. Finally, the chemisorbed NH_3 was desorbed in a N_2 flow by increasing the temperature up to 500 °C with a heating rate of 10 K/min. The ammonia desorbed was bubbled through a solution of sulfuric acid. The acid in excess was titrated with a solution of NaOH, the amount of ammonia desorbed being then calculated.

2.2 Esterification Reactions

The esterification reactions of acetic acid (Chimactiv, 99.5%) with *n*-butanol (Riedel-de Haën, 99.5%) were performed in a 150 mL two-neck flask equipped with a condenser and an additional port for sample withdrawal. The above assembly was heated using a thermostated hotplate. The reaction was carried out at 100 °C with a molar quantity of acetic acid of 0.09 and an *n*-butanol-to-acetic acid molar ratio varied from 1 to 3. Cyclohexane (Riedel-de Haën, 99.5%) was always added to the reaction mixture for water removal, the cyclohexane-to-acetic acid molar ratio being kept at 1. The amount of catalyst was varied between 0.5 and 1.0% of the mass of mixture charge in the reaction and the reaction time varied between 30 and 120 min. Unless specified, all experiments were conducted at a speed of agitation of 600 rpm. All the catalysts used in the reaction were in the powder form. Samples from the organic layer were withdrawn at regular intervals and analyzed with a Thermo Finnigan chromatograph using a DB-5 column and a flame ionization detector. Under the employed conditions of reaction, both in the presence and in the absence of a catalyst, butyl acetate was the only product detected. The mass balances, calculated after a reaction time of 120 min, were always higher than 94%.

3 Results and Discussion

3.1 Catalysts Characterization

Figure 1 shows the XRD patterns of the supported catalysts and the alumina support. Only broad lines corresponding to γ-alumina (PDF 10-425) were observed in all cases suggesting that MoO_x species are well dispersed on the alumina support.

The surface areas and the pore volumes of the catalysts are given in Table 1. The surface area and the total pore volume of the samples decreased by dispersing MoO_3 on alumina and by increasing its content. The reduction in surface area and pore volume has already been observed for alumina-supported molybdenum oxide [10] and may be due to the blockage of pores by MoO_x species. The supported samples possess high surface areas due to the dispersion effect of porous carrier.

A key point to understand the catalytic behavior in an acid-catalyzed reaction deals with the identification of the acid function of the materials. This was achieved using the NH_3-TPD technique. The total acidities of the catalysts, expressed as the total number of acid sites per gram of catalyst, determined by NH_3-TPD, are presented in Table 1. It can be observed that the total acidity is higher for the supported samples than for the alumina support and increases with increasing the MoO_3 loading. Nevertheless, we note that the desorption of all the adsorbed ammonia took place at temperatures lower than 350 °C in the case of both supported molybdenum oxide samples while in the case of alumina support the temperature has been raised up to 500 °C for the desorption of all the adsorbed ammonia. This suggests that the supported molybdenum oxide

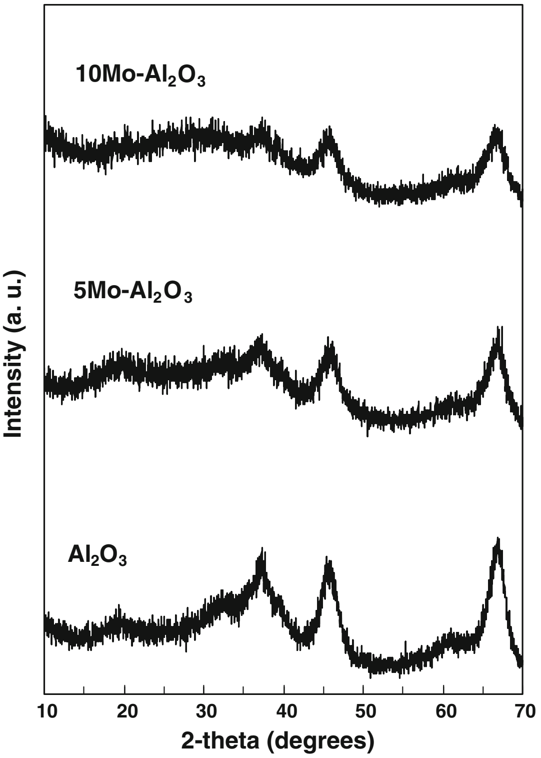

Fig. 1 X-ray diffraction patterns of the alumina support and of the alumina-supported MoO$_3$ catalysts

Table 1 Physico-chemical properties of the catalysts

Catalyst	BET surface area (m^2/g)	Total pore volume (cc/g)	Total acidity (mmol/g)
Al$_2$O$_3$	227	0.38	0.12
5Mo–Al$_2$O$_3$	196	0.35	0.36
10Mo–Al$_2$O$_3$	178	0.30	0.52

samples exhibit only weak and medium strength acid sites while alumina support also exhibits high strength acid sites.

3.2 Catalytic Activity

3.2.1 *Influence of the Reaction Time*

The influence of the reaction time was studied in the following reaction conditions: 8 mL of *n*-butanol, 5 mL of acetic acid and 10 mL of cyclohexane; the catalyst represents 0.7% of the mass of mixture charge in the reaction; the reaction temperature was kept at 100 °C. In these conditions, the selectivity of *n*-butyl acetate was, in all cases, 100%. This means that the conversion of acetic acid can represent the yield of *n*-butyl acetate.

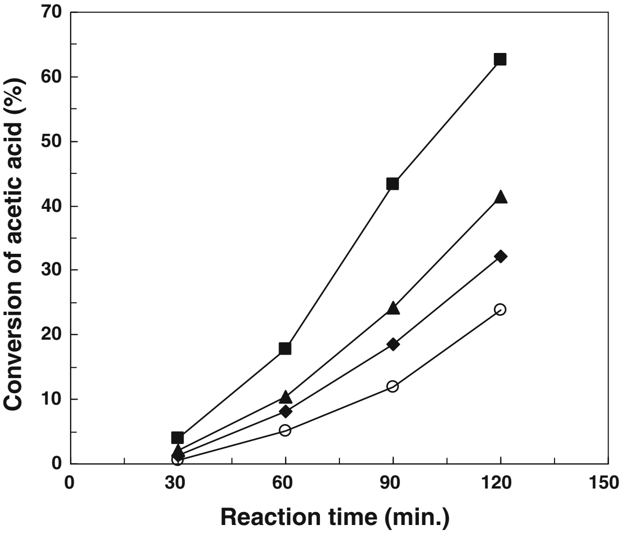

Fig. 2 Conversion of acetic acid as a function of the reaction time in the catalytic and non-catalytic reaction. Reaction conditions: molar ratio acetic acid:*n*-butanol = 1:1, reaction temperature 100 °C, 0.7 wt% catalyst. (*circle* non-catalytic reaction, *diamond* Al$_2$O$_3$, *triangle* 5Mo–Al$_2$O$_3$, *square* 10Mo–Al$_2$O$_3$)

The conversion of acetic acid measured in the above reaction conditions as a function of the reaction time over Al$_2$O$_3$, 5Mo–Al$_2$O$_3$ and 10Mo–Al$_2$O$_3$ catalysts as well as in the absence of a catalyst is shown in Fig. 2. As expected, the conversion of acetic acid was higher in the presence of a catalyst than without a catalyst and increased remarkably with the prolonging of the reaction time. The activities at 120 min of reaction time are compared in the following. As known, esterification is a typical acid catalyzed reaction, and the acidity of the catalyst would exert a great influence on the catalytic activity. The highest conversion (62.6%) of acetic acid over 10Mo–Al$_2$O$_3$ catalyst may thus be due to its high acid site density (Table 1) comparatively with 5Mo–Al$_2$O$_3$ (conversion 41.4%) and Al$_2$O$_3$ (conversion 32.2%) catalysts that have lower acid site densities. Nevertheless, when the site-time yields (STY, mol/mol H$^+$/s), are compared, the alumina support shows an activity higher (STY = 0.246 mol/mol H$^+$/s) than 5Mo–Al$_2$O$_3$ and 10Mo–Al$_2$O$_3$ samples for which STY are 0.105 and 0.110 mol/mol H$^+$/s, respectively. This is in line with the fact that γ-alumina possesses stronger acid sites than the supported molybdenum oxide samples, as shown from the NH$_3$-TPD experiments.

3.2.2 *Influence of the Molar Ratio of Reactants*

The effect of mole ratio of reactants on the esterification of acetic acid with *n*-butanol for catalytic and non-catalytic reactions is presented in Fig. 3. For all acetic acid to *n*-butanol mole ratios, the only product observed was *n*-butyl acetate. With the increase in *n*-butanol to acetic acid mole ratio from 1:1 to 2:1 and to 3:1, the conversion increased in all cases because, as expected based on the Le

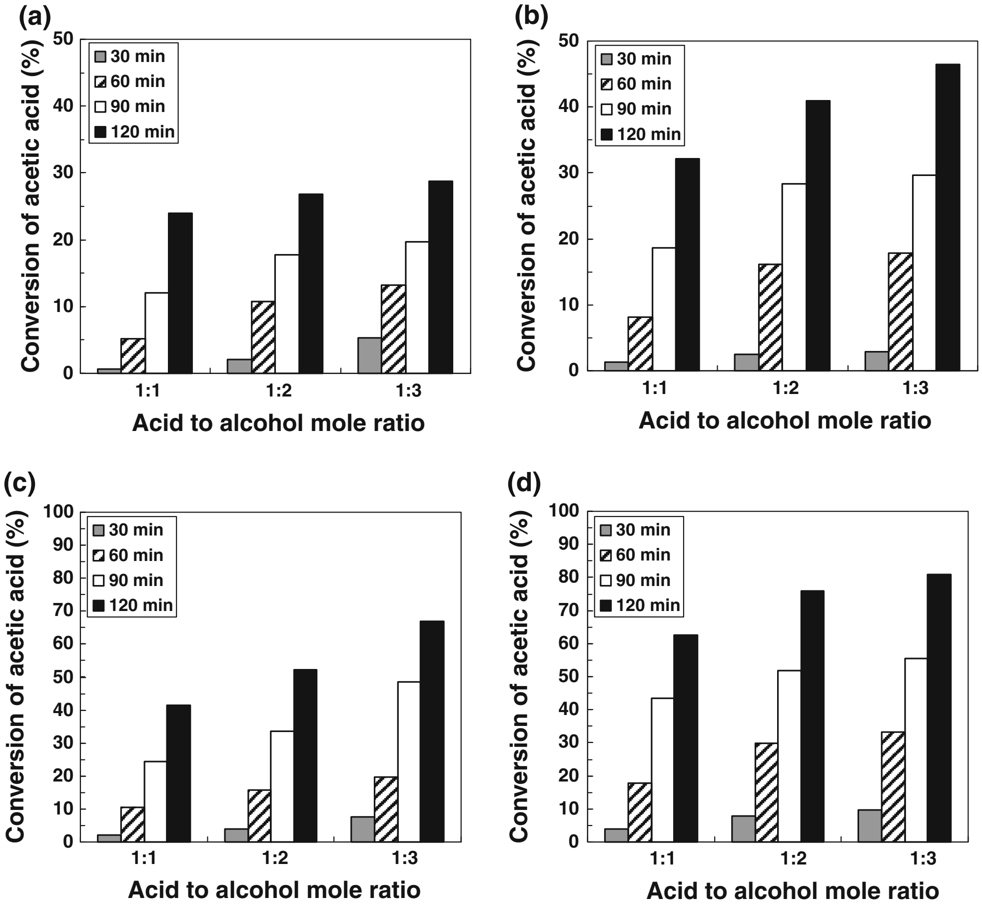

Fig. 3 Effect of mole ratio on the esterification of acetic acid with *n*-butanol in the non-catalytic reaction (**a**) and using Al_2O_3 (**b**), 5Mo–Al_2O_3 (**c**) and 10Mo–Al_2O_3 (**d**) as catalysts. Reaction conditions: temperature 100 °C, 0.7 wt% catalyst

Châtelier principle, the increase of the alcohol amount enhances the conversion of the acid. The conversion of acetic acid reached 81% in the presence of 10Mo–Al_2O_3 catalyst for an *n*-butanol to acetic acid mole ratio equal to 3:1 and a reaction time of 120 min.

3.2.3 Influence of the Speed of Agitation

The influence of the speed of agitation on the conversion of acetic acid was carried out for Al_2O_3 and 10Mo–Al_2O_3 catalysts samples at three different speeds 450, 600 and 750 rpm to examine the influence of an external mass transfer effect under the following reaction conditions: *n*-butanol to acetic acid mole ratio was 1:1, 0.7 wt% catalyst, reaction temperature 100 °C and reaction time 60 min. The results obtained are shown in the Fig. 4. It is clear from the figure that for both catalysts there was no effect of the speed of agitation in the range 450–750 rpm on the conversion of acetic acid. This implies that there was no resistance to mass transfer of acid to the external surface of the catalyst.

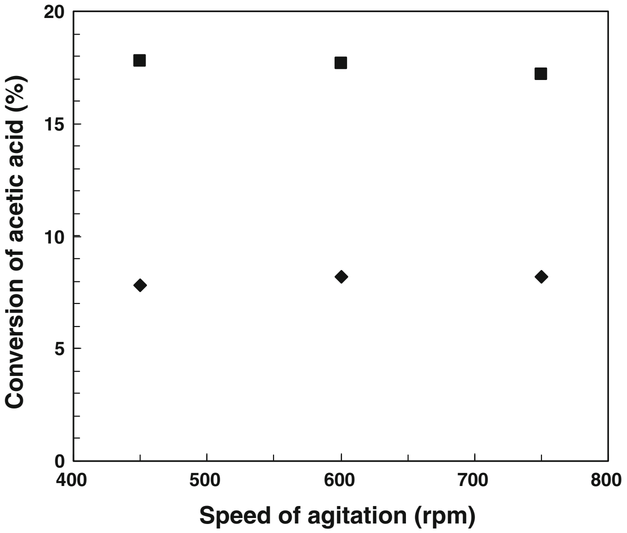

Fig. 4 Effect of the speed of agitation on the conversion of acetic acid for Al_2O_3 (*diamond*) and 10Mo–Al_2O_3 (*square*) catalysts. Reaction conditions: molar ratio acetic acid:*n*-butanol = 1:1, reaction temperature 100 °C, 0.7 wt% catalyst, reaction time 60 min

3.2.4 Influence of the Mass Fraction of the Catalyst

The effect of the catalyst concentration on the esterification of acetic acid with *n*-butanol for Al_2O_3 and 10Mo–Al_2O_3 samples at 60 and 120 min is shown in Fig. 5. The mass fraction of the catalyst was 0.5, 0.7 and 1.0% of the total reaction mixture. It can be observed, in all the cases studied, an increase of the conversion of acetic acid with the mass fraction of the catalyst, more attenuated when the mass fraction of the catalyst was increased from 0.7 to 1%. The conversion tends to a plateau for mass fractions of the catalyst around 1%. This means that the optimal mass fraction of the catalyst in the reaction medium is around 1%.

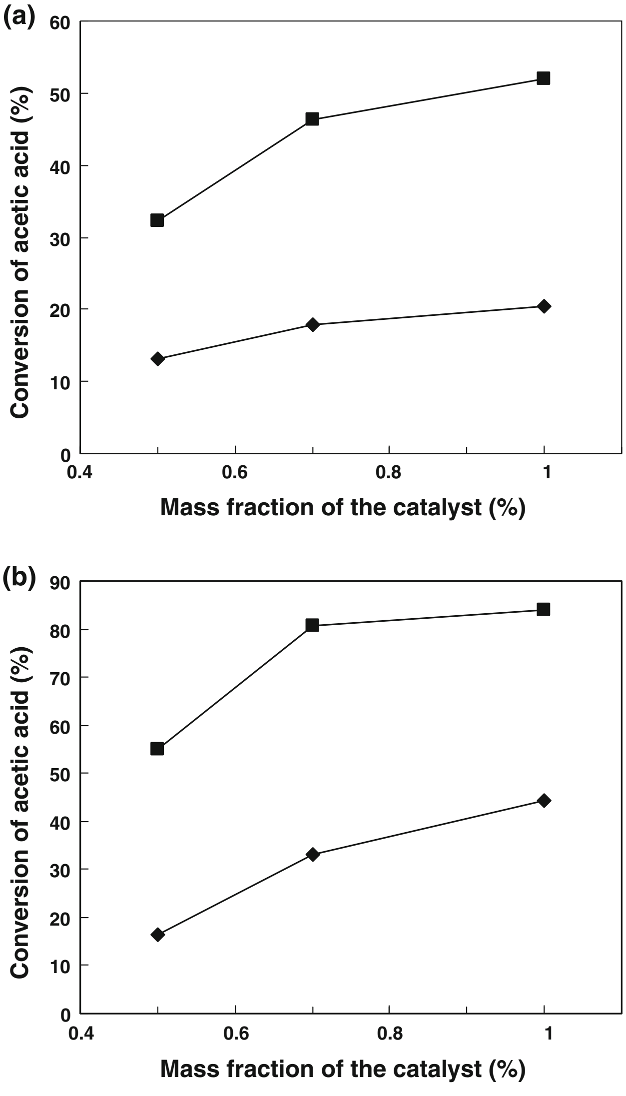

Fig. 5 Effect of catalyst concentration on the esterification of acetic acid with *n*-butanol using Al_2O_3 (**a**) and 10Mo–Al_2O_3 (**b**) as catalysts. Reaction conditions: temperature 100 °C, molar ratio acetic acid:*n*-butanol =1:3. (*diamond* 60 min, *square* 120 min)

Table 2 Reusability of the 10Mo–Al_2O_3 catalyst in the esterification of acetic acid with *n*-butanol

Cycle	Reaction time (min)	Conversion (%)	Selectivity (%)
First	30	3.9	100
	60	17.7	100
	90	43.4	100
	120	62.6	100
Second	30	3.8	100
	60	18.0	100
	90	44.5	100
	120	61.6	100
Third	30	4.1	100
	60	17.6	100
	90	43.8	100
	120	62.3	100

Reaction conditions: *n*-butanol to acetic acid mole ratio = 1:1, 0.7 wt% catalyst and reaction temperature 100 °C

3.2.5 Reusability of the Catalyst

The used 10Mo–Al_2O_3 catalyst in the first cycle of the reaction was separated by filtration and dried in an oven at 120 °C overnight. It was then used for the esterification of acetic acid with *n*-butanol with a fresh reaction mixture under the following reaction conditions: *n*-butanol to acetic acid mole ratio equal to 1:1, 0.7 wt% catalyst and reaction temperature 100 °C. The procedure was repeated after the second cycle. The results obtained are presented in Table 2. From these results, it can be concluded that the catalyst can be reused as there is no loss in catalytic activity and product selectivity during the three cycles.

4 Conclusion

Molybdenum oxide supported on γ-alumina acts as an efficient stable solid acid catalyst for the esterification of acetic acid with *n*-butanol. In all the esterification reactions the selectivity was 100% while the conversion reached about 81% in the presence of 10Mo–Al_2O_3 sample within 120 min of reaction time for an *n*-butanol to acetic acid mole ratio equal to 3 at 100 °C. The conversion increased in the following order: Al_2O_3 < 5Mo–Al_2O_3 < 10Mo–Al_2O_3 in line with the total acid site density measured by NH_3-TPD. The optimal mass fraction of the catalyst in the reaction medium was around 1%. The catalytic properties of the 10Mo–Al_2O_3 catalyst are maintained after three successive reactions.

References

1. Kirk-Othmer (1994) Encyclopedia of chemical technology, 4th edn., vol 9. Wiley, New York, p 755

2. Sawant DP, Vinu A, Justus J, Srinivasu P, Halligudi SB (2007) J Mol Catal A Chem 276:150
3. Liu Y, Lotero E, Goodwin JG Jr (2006) J Catal 242:278
4. Izci A, Bodur F (2007) React Funct Polym 67:1458
5. Corma A, Garcia H, Iborra S, Primo J (1989) J Catal 120:78
6. Zhang HB, Zhang BZ, Li HX (1992) J Nat Gas Chem 49:56
7. Timofeeva MN, Matrosova MM, Il'inich GN, Reshetenko TV, Avdeeva LB, Kvon RI, Chuvilin AL, Budneva AA, Paukshtis EA, Likholobov VA (2003) Kinet Catal 44:778
8. Zhang F, Wang J, Yuan C, Ren X (2006) Sci China Ser B Chem 49:140
9. Bhorodwaj SK, Pathak MG, Dutta DK (2009) Catal Lett 133:185
10. Chen K, Xie S, Bell AT, Iglesia E (2001) J Catal 198:232