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Study of Catalysts on the Synthesis of Methyl Acrylate by Hydroesterification of Methyl Formate with Acetylene

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Abstract: The catalytic hydroesterification of methyl formate (MF) with acetylene to methyl acrylate (MA) over nickel-based catalysts prepared by impregnation has been comprehensively studied in a fixed bed reactor at 160~240℃ and under 4~6MPa, GHSV: 630h^{-1}, CO:N_2:C_2H_2= 65:28:7. In present work, we have found a catalyst of 11wt%NiO/Al_2O_3 (80~100 mesh) prepared by wet impregnation with $NiCl_2$ aqueous solution, then calcined in air at 500℃ for 5 h. The selectivity to methyl acrylate and the conversion of methyl formate over 11wt%NiO/Al_2O_3 catalyst are higher than other catalysts studied in this paper. The optimum reaction temperature for the hydroesterification of methyl formate with acetylene to methyl acrylate is around 220℃.

Keywords: Ni-based catalyst, methyl formate, methyl acrylate, acetylene.

Nickel-based catalysts are widely used in the chemical industry, such as in hydrogenation, steam reforming, and methanation reactions[1]. The catalytic performances of nickel catalysts are sensitive to preparation methods, supports and promoters[2]. The catalytic conversion of methyl formate to methyl acrylate is a very interesting process, in which, *via* methyl formate, the transport and handling CO/CH_3OH at locations where the latter are difficult to obtain or to handle can be simplified[3].

Nickel-based catalysts were prepared by wet impregnation using one of $Ni(NO_3)_2$, $NiCl_2$, $NiBr_2$, $NiSO_4$ or $Ni(AC)_2$ aqueous solution with selected support (Al_2O_3, activated carbon, silica, TiO_2, CaA, or silica gel), and followed by calcination in air.

The activity and selectivity of nickel catalysts for the hydroesterification of methyl formate with acetylene to methyl acrylate were investigated in a flow stainless steel fixed-bed reactor (φ0.78cm×40cm) equipped with temperature controllers and monitors. The reactor wall and zeolite used for supporting the catalyst proved inert to the reactant studied. Acetylene dissolved in methyl formate was simultaneously pumped into the high-pressure reaction system. In all cases, the amount of catalyst used was 1.3g. The analysis of the product was preformed with SC-1001 chromatograph equipped with a modified GDX 103 packed column and TCD (thermal conductivity detector). The analysis conditions were: rate of carrier gas H2, 20ml/min; column temperature, 155℃; thermal conductivity detector temperature, 100℃; injection temperature, 220℃; and current, 100mA.

The gaseous products analyzed throughout the whole work show that only CO, N_2, CO_2 and unreacted C_2H_2 were detectable by GC under the above reaction conditions.

Results and Discussion

1 Effect of NiO content on the performance of NiO/Al_2O_3 catalysts

Table 1 indicates that over 9.9wt%NiO/Al_2O_3 catalyst, the selectivity to methyl acrylate reached the maximum, and the methyl formate conversion is a little lower than that over 12.2wt% NiO/Al_2O_3, which suggests that the content of NiO over NiO/Al_2O_3 suitable for the hydroesterification of acetylene is about 10wt.%.

Table 1 Effect of Nickel content on the performance of NiO/Al_2O_3 catalysts

Catalyst	NiO content (%)	Conversion of MF (%)	Selectivity to MA(%)
AX-1	0.8	51	19
AX-2	2.3	56	16
AX-3	9.9	59	32
AX-4	12.2	61	22
AX-5	14.2	54	19
AX-6	18.7	52	20

Reaction conditions: C_2H_2: MF=0.5~0.8:1, T=220℃, P=5.5~6 MPa.
Note. Catalysts (60~80 mesh) were prepared by wet impregnation with $Ni(NO_3)_2$ aqueous solution of selected concentration for a giving desired nickel content, dried in air at 120℃ for 3 h, and followed by air-calcining at 500℃ for 5 h.

2 Effect of support on the hydroesterification of acetylene

As shown in **Table 2**, the conversion of methyl formate but not the selectivity of methyl acrylate is well related to the specific surface area of the catalyst supports. The highest selectivity to methyl acrylate is achieved over the support of γ-Al_2O_3, however, its specific surface area is not the largest. Obviously, besides the specific surface area of the support, there are some other physicochemical properties affecting the performance of reaction.

Table 2 Effect of support on the hydroesterification of acetylene

Support	Specific surface area (m^2/g)	Conversion of MF (%)	Selectivity to MA (%)
$\gamma-Al_2O_3$	287	60	52
C	554	65	37
Silica	16	59	24
TiO_2	49	49	27
CaA	353	64	24
Silica gel	421	63	16

Reaction conditions: NiO contents are 11wt%, C_2H_2: MF=1.6~2:1, T=220℃, P=5~5.5 MPa.
Note. Catalysts (60~80 mesh) were prepared by wet impregnation with $Ni(NO_3)_2$ aqueous solution, dried in air at 120℃ for 3 h, and followed by air-calcining at 500℃ for 5 h.

3 Effect of precursor on the performance of 11wt%NiO/Al_2O_3 catalyst

Effect of the hydrated precursors of nickel on the catalytic performance was illustrated in **Table 3**. The nickel precursor used has significant influence on the reaction behavior. The highest selectivity to methyl acrylate was obtained by using nickel chloride as the precursor, however, the highest conversion of methyl formate can be achieved by using nickel bromide as the precursor, which suggests that the negative anion composed of nickel precursor plays an important role in determining the performance the NiO/Al_2O_3 catalyst.

Table 3 Effect of precursor on the performance of 11wt%NiO/Al_2O_3 catalyst

Catalysts precursor	Conversion of MF (%)	Selectivity to MA (%)
$Ni(NO)_2$	60	47
$NiCl_2$	45	69
$Ni(OAc)_2$	72	10
$NiSO_4$	64	36
$NiBr_2$	78	36

Reaction conditions: C_2H_2:MF=1.2~1.5:1, T=220℃, P=5~5.5 MPa.
Note. Catalysts (60~80 mesh) were prepared with the procedure same as in **Table 2**.

4 Effect of temperature on the performance of 11wt%NiO/Al_2O_3 catalyst

Effect of temperature on the reaction behavior is shown in **Table 4.** The conversion of methyl formate was significantly enhanced with the increase of the reaction temperature in the range of 160 to 240℃, however, there exists an appropriate reaction temperature for the selectivity to methyl acrylate.

Table 4 Effect of temperature on the performance of 11wt%NiO/Al_2O_3 catalyst

Reaction temperature (℃)	Conversion of MF (%)	Selectivity to MA (%)
160	13	4
180	33	5
200	35	23
220	52	47
240	85	32

Reaction conditions: C_2H_2:MF=1~1.2:1, T=220℃, P=4~4.5 MPa.
Note. Catalysts (60~80 mesh) were prepared with the procedure same as in **Table 2** using $NiCl_2$ precursor and calcined at 400℃ for 5 h in air.

5 Effect of particle size on the performance of 11wt%NiO/Al_2O_3 catalyst

Catalyst particle size affected the catalytic performance of 11wt%NiO/Al_2O_3 as shown in **Table 5.** The highest selectivity to methyl acrylate and the higher conversion of methyl formate have been achieved over the studied catalyst with the particle size between 80~100 mesh.

Table 5 Effect of particle size on the catalytic performance of 11wt%NiO/Al_2O_3 catalyst

Particle size (mesh)	Conversion of MF (%)	Selectivity to MA (%)
20~40	27	41
40~60	21	37
60~80	39	49
80~100	38	75
>100	12	23

Reaction condition: C_2H_2:MF=0.8~1:1, T=220℃, P=4~4.5 MPa.
Note. Catalysts were prepared with the procedure same as in **Table 2** using $NiCl_2$ precursor.

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